



3.0 WVDP

This write-up was provided by WVDP and inserted with minimal revisions.

NUCLEAR FUEL SERVICES HISTORICAL OVERVIEW AT WEST VALLEY

To ensure a self-sufficient, domestic commercial nuclear power industry, the AEC encouraged the transfer of nuclear fuel reprocessing from the federal government to private industry. As a result of this policy, three commercial reprocessing facilities were built in the U.S.: General Electric's Midwest Fuel Recovery Plant at Morris, Illinois; Allied General Nuclear Services (AGNS) plant at Barnwell, South Carolina; Nuclear Fuel Service's facility located near West Valley, New York.

Optimism about the future growth of the nuclear industry led the State of New York to set aside 3,345 acres near West Valley, New York, and to encourage nuclear industries to locate there. Although fuel reprocessing had been practiced in the U.S. since 1944, large-scale fuel reprocessing in the U.S. had been conducted only at DOE facilities in Idaho, South Carolina, and Washington State, until NFS began operations at West Valley, NY.

The NFS West Valley facility was the first and only private plant in the U.S. to reprocess spent nuclear fuel. The NFS facility was a PUREX (Plutonium Uranium Extraction) process plant with a design capacity of 300 tons of fuel per year. The PUREX process included storing spent fuel assemblies; chopping the assembly rods; dissolving the uranium, plutonium, and radioactive products in acid; separating and storing the radioactive wastes, and separating uranium nitrate from plutonium nitrate.

In the spring of 1963, the AEC issued the necessary permits to NFS, a subsidiary of the W.R. Grace Company (NFS was acquired by the Getty Oil Company in 1969), to begin construction of a fuel reprocessing facility. NFS was granted a license on May 27, 1965 to receive and store fuel at its reprocessing facility in West Valley. The first shipment of fuel, from the Yankee Rowe reactor in Massachusetts, was placed in the fuel storage pool at West Valley on June 5, 1965. Government and commercially-generated fuel continued to be received at NFS until 1973. There were a total of 756 truck and rail shipments.

The AEC encouraged NFS to focus on commercial fuel reprocessing; however, the AEC guaranteed a minimum quantity of government fuel to NFS in the absence of sufficient commercial supplies. Sufficient commercial supplies were not available because there were not many operating commercial reactors during the NFS reprocessing period of 1966 to 1972. As a result, approximately 60 percent of



the facility's supply of fuel and 33 percent of the plutonium came from AEC reactors. Specifically, a majority of this came from N-Reactor, located near Hanford, Washington.

In 1972, NFS (now owned by the Getty Oil Company) halted all reprocessing operations in order to increase reprocessing capacity, and to alter the facility to meet new regulatory requirements. However, subsequent difficulties were encountered in retrofitting the facility to meet these requirements. After four years of fruitless negotiations with federal and state regulatory authorities, NFS announced its intention to cease reprocessing operations at the West Valley Site. The management and long-term storage of approximately 600,000 gallons of high-level radioactive liquids and sludge was transferred to the site's landlord, the New York State Energy Research and Development Authority. This transfer was in accordance with contractual obligations. By 1980, the West Valley Demonstration Project Act (WVDPA) (Public Law 96-368) directed the DOE to solidify the high-level radioactive waste at West Valley into a borosilicate glass that was suitable for permanent storage in an approved federal repository. The WVDPA also directed the Department to decontaminate and decommission the tanks and facilities used at West Valley, and dispose of the low-level and transuranic wastes.

The West Valley Nuclear Services Company, a wholly-owned subsidiary of Westinghouse Electric Company, was selected in 1981 as the prime contractor for the West Valley Demonstration Project (WVDP). West Valley Nuclear Services Company has managed and operated the West Valley site for the U.S. Department of Energy since 1982. West Valley Nuclear Services is a Westinghouse Government Services Group company.

Site Description

The site is located in Cattaraugus County, New York, on the Western New York Nuclear Services Center. It is now referred to as the West Valley Demonstration Project and is managed by the Department of Energy and operated by West Valley Nuclear Services. This location is about 35 miles south of Buffalo, New York.

Uranium Processing Facility - Main Processing Plant

Plant Description

The only processing activity at the NFS facility in West Valley occurred in the Main Processing Plant. The plant was designed to facilitate the remote handling of spent reactor fuel and to separate and recover the uranium and plutonium. Fission products were separated from the product material and processed as liquid waste materials. The PUREX (plutonium uranium extraction) process was utilized for the recovery of uranium and plutonium. The PUREX process utilized pulsed solvent extraction columns with a counter



current flow of tributyl phosphate and kerosene. This organic solvent picks up the plutonium and uranium nitrates and the fission products remain and are removed in the aqueous phase. The recovered materials are extracted and concentrated together in the organic solvent and then purified by chemical scrubbing with dilute nitric acid. Two further cycles of solvent extraction and scrubbing each result in separate, concentrated, and purified aqueous solutions of plutonium nitrate and uranium nitrate.

Material Flowsheet

(Attach color flowsheet - 900E - 7206 Rev 0) Processing Flow Chart

Feed Specification

The plant was designed to chemically separate the plutonium and uranium from reactor fuel. The PUREX process was utilized and plant was constructed to remotely handle all material because of high radiation readings encountered when performing this activity. Irradiated fuel was mainly processed at this plant although one batch of new fuel was reprocessed prior to running it through a reactor. Normally the feed (spent fuel) consisted of slightly enriched uranium.

Product Specifications

The design of the plant intended for 99.9 percent of the fission products to be separated from the recovered uranium and plutonium. These fission products would be retained in the liquid waste and processed as such in the plant facilities. The specifications and actual chemical analysis of each shipment are not available at the site.

Operating History

The Nuclear Fuel Services Plant at West Valley, New York, operated from 1966 to 1972. The last processing campaign ended in 1972 and the last product shipments were completed that same year.

Current Status

The Main Processing plant is presently undergoing decontamination and decommissioning activities. Support systems are currently being utilized to maintain some plant conditions and configurations.

Activity Summary

The West Valley Site is the former Western New York Nuclear Services Center. The site was operated by Nuclear Fuel Services a division of W.R. Grace Chemical Company. The site operated from 1966 to 1972 and was designed and operated to reprocess spent nuclear fuel assemblies from government and commercial reactors. The PUREX process was utilized to chemically separate and recover uranium and



plutonium from reactor fuel. A total of 620 metric tons of uranium was recovered and 619 tons of this was shipped to Fernald, Ohio, to the Feed Materials Production Center for additional processing.

RECYCLED URANIUM

Uranium Recycle Description

There were a total of 27 processing campaigns performed at West Valley, however, only the first 26 campaigns reprocessed intact reactor fuel. The last campaign involved processing liquid residues received from Nuclear Fuels Services Facility in Erwin, Tennessee, generated during the fabrication of fuel for the SEFOR reactor. Table D-2 provides a summary of the NFS fuel reprocessing campaigns including the amount of uranium recovered. The material reprocessed by NFS, summarized by source, was both government and commercially-generated. In both tables the quantities of "Uranium Received" were based on shipper's data, i.e., theoretical calculations of the uranium contained in the fuel.

Other factors that contribute to the difference between received and recovered uranium include the measurement uncertainty, process holdup, and normal operating losses/measured discards. Normal operating losses/measured discards occur when known quantities of uranium are intentionally removed from the inventory because they are technically or economically unrecoverable and are disposed of by approved methods. Two examples of normal operating losses are liquid discards to waste storage tanks, and solid waste packaged in drums and crates awaiting shipment to waste disposal facilities generically referred to as "burial sites." Examples of uranium-bearing items sent to burial sites include discarded piping, spent ion exchange equipment, and contaminated laundry and shoe covers.

The AEC-owned uranium originated at the following reactors:

The Hanford N-Reactor, a production reactor formerly called the New Production Reactor, is located near Richland, Washington, about 150 miles southeast of Seattle. This reactor is owned and was operated by the AEC. N-Reactor was designed as a dual-purpose reactor for the production of plutonium and the production of by-product steam for electricity generation. It was a graphite-moderated, pressurized light water-cooled reactor. N-Reactor operated from 1963 to 1987.

The Bonus Reactor, a demonstration boiling water reactor, was located at Rincon, about 75 miles west of San Juan, Puerto Rico. This reactor featured high-temperature, superheated steam and was owned by the AEC but operated by the Puerto Rico Water Resources Authority. The Bonus reactor began operation in 1964 and was permanently shut down in 1968.



The remainder of the material came from the Nuclear Fuels Services facility in Erwin, Tennessee, and was in the form of liquid residues generated during the fabrication of reactor fuel for the Southwest Experimental Fast Oxide Reactor (SEFOR), an experimental reactor, located near Strickler, Arkansas. SEFOR was built by the Southwest Atomic Energy Associates¹ for testing liquid metal fast breeder reactor fuel. SEFOR began operations in 1969 and was permanently shut down in 1972.

The remaining fuel came from seven commercial nuclear power reactors that were owned and operated by commercial utility companies.

The Big Rock Point Nuclear Power Plant. This boiling water reactor, owned and operated by Consumers Power Company, is located on Lake Michigan near Charlevoix, Michigan, about 200 miles northwest of Detroit. Big Rock Point has operated since 1963.

CVTR, Carolinas-Virginia Tube Reactor. This pressurized heavy water tube reactor, owned and operated by Carolinas-Virginia Nuclear Power Associates was located in Parr, South Carolina, about 25 miles northwest of Columbia. This reactor began operation in 1964 and was permanently shut down in 1967.

Dresden Nuclear Power Station, Unit #1. This boiling water reactor, owned and operated by Commonwealth Edison Company, was located near Morris, Illinois, about 50 miles southwest of Chicago. Dresden-1 commenced operation in 1960 and was permanently shut down in 1978.

Humboldt Bay Nuclear Plant. This boiling water reactor, owned and operated by the Pacific Gas and Electric Company, was located on Humboldt Bay near Eureka, California, about 200 miles north of San Francisco. This plant commenced operation in 1963 and was permanently shut down in 1976.

Indian Point Nuclear Power Station, Unit #1. This pressurized water reactor, owned and operated by the Consolidated Edison Company, was located on the Hudson River at Buchanan, New York, about 35 miles north of New York City. Indian Point Unit 1 began operation in 1962 and was permanently shut down in 1974.

¹ The Southwest Atomic Energy Associates consisted of seventeen U.S. investor-owned utilities, the Federal Republic of Germany, the General Electric Company, and Euratom. Euratom, the European Atomic Energy Community, is an organization that promotes the growth of nuclear power production in Europe. Its members are Belgium, France, West Germany, Italy, Luxembourg, and The Netherlands.



Pathfinder Nuclear Power Plant. This experimental, boiling water reactor, owned and operated by the Northern States Power Company, was located on the Big Sioux River, near Sioux Falls, South Dakota. Pathfinder began operations in 1964 and was permanently shut down in 1967.

Yankee Atomic Electric Power Station. A pressurized water reactor, owned by the Yankee Atomic Electric Company, was located near Rowe, Massachusetts, about 45 miles east of Albany, New York. Began operation in 1960 and was permanently shut down in 1992.

Uranium Receipts (N/A - Spent Fuel is out of scope for this Project)

Uranium Shipments

All material in the scope of this project was shipped as a liquid uranyl nitrate to Fernald for further processing. A total of 619 metric tons of material was shipped during the years of 1966 to 1972.

Recycle Uranium Waste

All waste from the NFS campaigns associated with the West Valley Site are identified, controlled, and will be eventually dispositioned in accordance with the West Valley Demonstration Act, Public Law 96-368. Presently a Record of Decision on the final decommissioning of the site is in progress of being negotiated with the public and stakeholders.

Recycle Uranium Scrap (N/A)

There is no inventory or uranium scrap at the site. All material that was processed here was shipped for further processing. Overall Recycled Uranium Site Material Balance

All uranium that falls into the scope of this category has been detailed in the tables. No material is presently on site that remains under the scope of this Project. All in project scope uranium material processed at West Valley was sent to Fernald for further processing. See tables for complete accounting.

CONTAMINANTS IN RECYCLED URANIUM (N/A)

There are no analytical records or accounting of West Valley processed fuel. Since all material processed here was shipped to Fernald, the analytical accounting of this material will be part of their overall Recycled Uranium Shipments. All material processed at West Valley was shipped to Fernald as a liquid uranyl nitrate for further processing.

CURRENT INVENTORY (N/A)

There is none of this material at the West Valley Site



TABLE D-2

FUEL REPROCESSED AND URANIUM RECOVERED AT WEST VALLEY

Lot No	Fuel Source	Reactor Name	Process Date	MTU	
				Received	Recovered
1	Atomic Energy Commission	N-Reactor	4-22-66	19.7	19.3
2			5-20-66	28.8	28.7
3			7-15-66	46.7	46.3
4	Commonwealth Edison	Dresden-1	11-12-66	50.0	49.6
5	Yankee Atomic Electric	Yankee Rowe	6-7-67	49.8	49.4
6	Atomic Energy Commission	N-Reactor	9-2-67	26.6	
7			12-2-67	26.1	
8			1-6-68	42.4	
9			5-5-68	38.8	
10			6-29-68	55.3	186.6
11	Consolidated Edison	Indian Point-1	11-15-68	1.1	0.9
12	Atomic Energy Commission	N-Reactor	2-13-69	48.9	48.5
13	Yankee Atomic Electric	Yankee Rowe	5-14-69	19.6	19.6
14	Atomic Energy Commission	N-Reactor	8-16-69	30.3	30.0
15	Commonwealth Edison	Dresden-1	10-1-69	21.5	21.7
16	Consolidated Edison	Indian Point-1	11-23-69	15.6	15.4
17	Yankee Atomic Electric	Yankee Rowe	6-2-70	9.3	9.2
18	Northern States Power	Pathfinder	8-14-70	9.6	9.6
19	Consumers Power	Big Rock Point	11-26-70	18.4	18.3
20	Consolidated Edison	Indian Point-1	1-11-71	7.6	7.5
21	Atomic Energy Commission	N-Reactor	2-25-71	15.8	15.5
22	Puerto Rico Water Resources Authority	Bonus	4-15-71		
		Superheater	4-18-71		
		Bonus Boiler		1.72.4	4.3
23	Pacific Gas and Electric	Humbolt Bay	5-20-71	20.8	20.7
24	Yankee Atomic Electric	Yankee Rowe	7-16-71	9.5	9.5
25	Carolinas-Virginia Nuclear Power Associates	CVTR-PARR	10-4-71	3.5	3.3
26	Consumers Power	Big Rock Point	11-30-71	5.8	6.0
27	Nuclear Fuels Services, Erwin, Tennessee	SEFOR	12-12-71	0.1	0.1
Total				625.7	619.9

IV DETAILED PROCESS DESCRIPTION

4.1 In this section the entire processing sequence is described in some detail starting with the introduction of fuel into the plant from a shipping cask and carrying it through the process step by step to the shipment of final products. The description is based upon the handling of the base-line fuel: low enriched UO_2 in stainless steel or zircaloy tubes. With the exception of some modifications to the head end treatment, the same flowsheets used for low-enriched UO_2 fuels are also used for SCRUP fuels (natural uranium clad in aluminum). At the conclusion of each subsection the differences in the process necessary to handle each of the following fuels are noted:

- a. $\text{ThO}_2\text{-UO}_2$ in stainless tubing, average 8% U (93.5% enriched)--Indian Point Core A
- b. U-Mo alloy in Zr, 25% U 235--Fermi Core A
- c. Enriched Uranium-Aluminum alloy clad in Aluminum--MTR
- d. U-3% Mo Alloy 1.6% enriched clad in aluminum-Piqua
- e. Enriched uranium-zirconium alloy clad in zirconium or zircaloy.

A process diagram for the base line fuel and for each of the above fuels is shown in Figure 4.21a. Flow rates and stream compositions for each fuel is given in Table 4.2.

Fuel Receiving and Storage

4.2 Fuel is received at the plant in shielded casks which will arrive on specially designed railroad flatcars and flat bed trailers. The larger casks will be cooled with demineralized water. Each shipment must conform at the time of shipment to 10 CFR Part 72, 49 CFR Parts 71-78 and to the Cask Acceptance Criteria shown in Appendix 4.2.

4.3 The cask and car or trailer are brought inside the building and monitored. Road dirt is removed by hosing and additional decontamination is carried out, if necessary. The cask temperature is recorded, the cask coolant is circulated and sampled, and any gas pressure in the cask is relieved and purged into the ventilation off-gas system.

Revision 1, October 29, 1962
Revision 2, May 30, 1964

4.4 The cask is then put into the cask unloading pool by the 100-ton overhead crane. The unloading pool contains demineralized water to a depth of 44 feet. The cask lid is removed using extension wrenches and the 5-ton hoist on the overhead crane. The fuel elements are then lifted out of the cask with grapples attached to the 5-ton hoist and loaded into storage cans which are in temporary storage racks in the unloading pool. The 5-ton hoist has a limit switch which will prevent the fuel element from rising above a level 11 feet below the water surface. The crane operator must maintain a pressure on the crane controls in order for the crane to operate. The empty cask is transferred to the cask decontamination pit for additional cleanup and preparation for shipment. After it is monitored the cask is reassembled and taken to the storage area for routine maintenance before it is shipped out.

4.5 The storage cans containing fuel elements are then transferred to the fuel storage pool. This is done with the storage pool crane which has a limited vertical lift so that a minimum of 11 feet of water shielding is maintained at all times. Only one storage can may be handled at a time. The storage racks are so spaced such that a critical condition cannot arise even when two of the most reactive arrays are stored adjacent to each other or when one such array passes another, as closely as possible, in the unloading operation. The location of each fuel element is carefully recorded in a log. A special basket tagging system is used for each fuel to avoid mixup. The tags are designed to be clearly visible under water. All storage cans and fuel movements are controlled by the shift supervisor.

4.6 Casks containing fuel elements known to be ruptured will have had those elements sealed in cannisters before shipment. Such cannisters are removed from the cask and placed in storage cans which are placed in racks in the unloading pool. These cannisters are purged into the ventilation off-gas system, if necessary. A hood leading to the ventilation off-gas system may be placed over the cannisters as they are stored until it is certain that the cannister is not leaking. They are then transferred into the regular storage racks.

4.7 If it is determined in the course of unloading a cask that an element has ruptured in transit, such an element will not be canned. The ruptured element will be placed, if necessary, in a special ruptured fuel cannister and treated as specified in Paragraph 4.6.

4.8 When it is desired to process a particular fuel, the shift supervisor will determine the location of this fuel from the log referred to in Paragraph 4.5. He will see that the desired elements (in their storage cans) are moved, one at a time, to the end of the fuel storage pool and affixed to the underwater transfer conveyor for transfer into the Process Mechanical Cell (PMC).

Revision 1, October 29, 1962
Revision 2, May 30, 1964

Mechanical Handling

4.9 The PMC which was described in Paragraph 3.11 contains equipment for mechanically disassembling and chopping the various fuel elements brought into the plant. Drawings of this area showing the various equipment pieces are shown in Figures 4.9a & 4.9b. A mechanical flow diagram is shown in Figure 4.9c. A list of the equipment included therein is shown in Table 4.9. The major equipment pieces are individually described in Section V.

4.10 To bring the fuel into the PMC from the storage pool it is first necessary to open the cover on the FRS hatch by a remotely operated air cylinder. The underwater transfer conveyor presents a loaded storage can at the hatch. The fuel element protrudes from the can sufficiently that a grapple attached to the PMC overhead crane is able to grab the element and lift it out of the storage can. The empty can is then returned to the fuel storage pool. The crane holds the fuel element over the hatch for the pool water to drain off. The hatch cover is then closed.

4.11 The fuel element is then placed in a tilting fixture and lowered on the inspection table, with the crane, for preliminary inspection and marking for the sawing operation. Other disassembly tasks are carried out, if required. Following this the fuel element is transferred by the crane to the saw table, using a fuel element carrier. The ends are then cut off with the saw. Other extraneous metal, such as tube sheets are cut off, if required. A slitting saw is mounted on the saw gantry to slit open the fuel element casing, if necessary. The sawed ends and pieces are placed in a scrap bucket. The casing is sawed into smaller sections at a later time and placed in a scrap bucket. The scrap buckets, when filled, are transferred to the General Purpose Cell through a hatch. The hatch cover is removed and replaced by the crane.

4.12 The fuel bundle is pushed out of its casing into a shear feed magazine by the pushout ram. The shear feed magazine is clamped to the saw table in line with the fuel element.

4.13 The shear feed magazine is picked up from the saw table and placed in the receiving station of the fuel bundle shear using the crane. The feed mechanism is moved forward until the magazine is sealed in place. It continues to move forward and pushes the forward end of the fuel element bundle against the movable blade of the shear.

4.14 Before chopping the fuel can begin, it is necessary to place an empty chopped fuel basket under the discharge chute of the fuel bundle shear. This operation is done in the General Purpose Cell (GPC) which is below the PMC. The discharge chute of the fuel bundle shear extends down through the ceiling of the GPC. An empty chopped fuel basket with a consumable liner inside it, is removed from its storage rack with the GOC overhead crane and placed in a socket on the chopped fuel basket loading station. The socket is transferred to the discharge chute by a mechanism actuated by a hydraulic cylinder outside the cell with a shaft running through the shielding wall. The empty basket and liner is forced up against the discharge chute, sealing it to the chute. There are 3 different sets of chopped fuel baskets with different diameters which are determined by the criticality parameter of the fuel being processed. (See paragraphs 6.118 through 6.126)

4.15 Prior to the chopping operation, the feed tube, shear chamber and discharge chute may be purged and blanketed with inert gas if required. The entire chopping operation may be carried out in an inert atmosphere. The fuel bundle is then sheared into pieces of preselected lengths one to two inches long, by the shear. The operation can be done manually or automatically and can be observed. The shear is driven by a hydraulic power unit and the fuel bundle is fed into the shear chamber by the feed ram.

4.16 Sodium-bonded fuels are not being considered within the present scope of design or in the present license application. If, at a later date, it is decided to include facilities in this plant too heavy to handle such fuels, the necessary facilities will be added at that time and a license amendment will be requested.

4.17 When the chopped fuel basket is filled a detector will automatically stop the shear. There is also a detector at the end of the discharge chute to stop the shear in case of a jam to guard against a criticality incident in the chute. The chopped fuel basket loading station is actuated to bring the fuel basket in reach of the crane. The crane with the fuel basket grapple transports the fuel basket to a storage rack. The baskets are cooled by forced air emanating from a cooling unit at the end of the rack. The racks are spaced to prevent criticality and a concrete wall prevents criticality caused by fuel baskets passing near the rack.

4.18 When it is time to charge the dissolver, the crane and grapple are used to remove a filled chopped fuel basket from the storage rack and transport it to the transfer station socket under the CPC hatch. It then picks up the basket with the leached hulls from the other transfer station socket and transfers it to the leached hull dumping, sampling and inspection station. The dumping mechanism which is actuated by a hydraulic cylinder outside the cell dumps the leached hulls from the basket into a hopper. After the necessary inspection and sampling the hulls are dumped into a scrap bucket. The empty basket is returned to an empty basket storage rack.

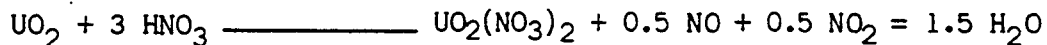
4.19 The cover on the hatch in the Chemical Processing Cell is removed using the CPC crane. The cover of the desired dissolver barrel is removed using the CPC crane. The crane hook with grapppler is inserted into the barrel and automatically fastens to the chopped fuel basket containing the leached hulls. It is withdrawn and transported to the CPC hatch and lowered down through the hatch into the General Purpose Cell and deposited in the transfer station socket. The grapppler is released and inserted into the filled chopped fuel basket which is next to the basket containing the leached hulls. The filled basket is then raised up through the hatch and transported to the dissolver and inserted into the selected barrel. The grapppler is released and the cover is replaced on the dissolver barrel. This process is repeated until the dissolver is completely refilled.

4.20 When the scrap buckets are ready for burial, a shielded truck is backed into the Scrap Removal Area. The scrap bucket is transported to a position under the hatch to the Scrap Removal Area. The hatch cover is opened and the crane in the Scrap Removal Area lowers down into the General Purpose Cell and brings out a filled scrap bucket and places it in the cask on the shielded truck. When the cask is full, the hatch cover is closed. The cover is put on the cask and the outside of the cask and truck are decontaminated. The truck then transports the cask to the burial area. A shielded crane removes the scrap buckets from the cask and deposits them in a burial trench.

Dissolution

4.21 Figure 4.21a is a plant flow diagram of all of the process steps from dissolution through product handling showing auxiliary operations and interconnections. Table 4.21 gives compositions and flow ranges for the major process streams. The stream numbers in this table refer to the numbers encircled in the process lines given in Figure 4.21a. Figure 4.21b is a schematic diagram of dissolution and feed preparation. Throughout this section a series of these schematics are presented covering each of the process steps. On them the flows of the various products and the fission products are shown by color coding.

4.22 In the dissolver the uranium dioxide fuel is leached out of the hulls with boiling nitric acid. The cladding--stainless steel or zirconium--is not attacked. The reaction of uranium dioxide with nitric acid can be approximated by the equation:



The uranium is completely oxidized to the (VI) state and is present as hydrated uranyl ions. However, nitric acid does not oxidize plutonium to its highest state. The product is a mixture of Pu(IV), and Pu(VI).

Rev. 4, September 1969

Figure 4.21a

Plan Flow Diagram of All Process Steps From
Dissolution Through Product Handling

Drawing 4413 15R-A-5

In the irradiated fuel, elements of all the atomic numbers between 30 (zinc) and 66 (dysprosium) are present as fission products. Most of these are stable or are so short lived that they have decayed to stable isotopes during the fuel cooling period. These stable isotopes form, together with the corrosion products coming from the process vessels, a nonradioactive contamination of the uranyl nitrate solution. These inactive nuclides do not present as much of a processing problem as do the radioactive fission products. The nuclides belonging to Groups I, II, and III of the periodic table (isotopes of cesium, strontium, yttrium, and the lanthanides) have a straight forward solution chemistry. They all form simple hydrated ions in nitric acid solution. The remaining high activity nuclides, isotopes or zirconium, niobium, and ruthenium, exhibit very complex behavior. Zirconium is present in nitric acid solution as $Zr(IV)$, a species which is readily hydrolyzed. The hydrolysis is not completely understood but it is known that slow polynuclear equilibria are involved and that considerable amounts of polymers still exist at 3 to 5 M nitric acid at least for a zirconium concentration of 50 millimols. Even less is known about the chemistry of niobium. In the acid concentrations used in this process it is certainly present as $Nb(V)$ and possibly as NbO_2^+ . Ruthenium has the most complex chemistry of all the fission products. It exists in nitric acid solution as $Ru(III)$ and $Ru(IV)$ and sometimes as even higher oxidation states. Each of these gives a variety of complexes with NO , NO_3 , NO_2 and OH^- . Especially important is the nitrosylruthenium group, $RuNO_3$, as the nitrate complexes of this group are readily extracted by TBP. As expected for complexes of the platinum metals, those of ruthenium are often inert, i.e., the rate of formation is slow, and once formed they adjust themselves only slowly to new conditions of equilibrium. It is this kinetic behavior which is believed to cause the irregular and unpredictable behavior of ruthenium in solutions of dissolved fuel.

4.23 To carry out the dissolution, chopped fuel contained in the perforated baskets described in the foregoing sections is brought into the Chemical Process Cell as described in paragraphs 4.18 and 4.19. These baskets are 8" in diameter or smaller depending on enrichment and are 7' high. A full fuel charge varies from 300 to 2200 lbs. depending on the specific fuel. Each basket is picked up by the dissolver loading crane (CPC-3V-1) and deposited into one of the barrels of the dissolver being used. Details of the dissolvers (CPC-3C-1, -2) are given in Section V.

Revision 1, October 29, 1962
Revision 2, May 30, 1964

4.24 After chopped fuel is added to the dissolver, a pre-determined volume and concentration of nitric acid is pumped into the dissolver from hot acid batch tank (HAC-7D-12). Either recovered or fresh acid may be used. The amounts of fuel and acid charged to the dissolver are adjusted so that the final dissolver solution contains no more than 7.5 grams per liter of U-235. At the highest enrichment of these fuels this concentration of U-235 is critically safe in all geometrics and quantities and, in fact, allows a safety factor of two on critical concentration. Criticality control and the steps taken to insure this concentration is not exceeded, are discussed in more detail in Section VI.

4.25 After the baskets of chopped fuel are in the dissolver, the required quantity of acid is metered in as measured by the liquid level instruments. The lower air-sparger is turned on to mix the solution during dissolution. Cooling water flow to the reflux condenser is established and steam admitted into the dissolver heating surfaces. The dissolution reaction starts at about 90° C at which time the steam is turned off to keep the dissolution reaction from producing more off-gas than the system will handle and still maintain a negative pressure in the dissolver. After the reaction subsides steam is again admitted into the dissolver heating surfaces. Dissolution should be complete in less than 12 hours---the last 3 or 4 hours of which the dissolver contents will be heated to boiling. Complete dissolution is indicated by leveling out of the off-gas pressures and temperature-specific gravity indicators.

During dissolution the following quantities are recorded:

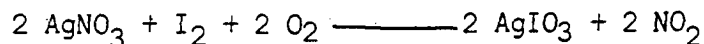
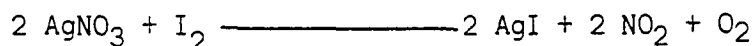
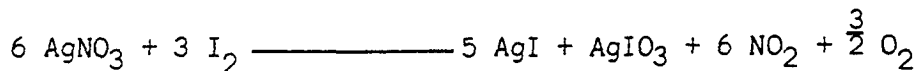
- (a) Specific gravity
- (b) Liquid level (with low alarms)
- (c) Pot temperature (Recorder-controller with high alarm)
- (d) Pressure (high alarm)
- (e) Off-gas temperature

Steam pressure to the heating jacket can be shut-off automatically by instrumentation if the system pressure reaches a pre-determined set point and cooling water can be introduced manually to the heating jacket. The dissolver can be sampled, if desired, but this will generally be done in the feed adjustment tank (CPC-3D-1).

4.26 During the course of the dissolution, off-gases are given off. The PID for the dissolver off-gas treatment is shown in Figure 6.3c under the discussion of ventilation. The treatment of this off-gas is shown schematically in Figure 4.26. The dissolver has a down-draft condenser so that some of the oxides of nitrogen are absorbed and returned

to the dissolver as nitric acid. The off-gas is then put through a scrubber (OGC-6C-6) and treated to remove iodine by first heating the gas to 200 C in the heater (OGC-6E-1) and then absorbing the iodine on silver nitrate coated ceramic Berl saddles in one of two silver reactors (OGC-6C-1, -1A). The gas is cooled (6E-2), sent through one of two parallel filters (OGC-6T-1, -1A), blowers (6V-1, -1A) and added to the general ventilation system for further filtration before discharge to the stack.

4.27 The silver reactors (OGC-6C-1, -1A) are the main items in the removal of radioactive components from the dissolver off-gasses. Each reactor is a packed column sized to give a superficial velocity of 1 foot per second at a length-to-diameter ratio of 4. The packing is unglazed ceramic Berl saddles which have been immersed in 18 to 20 M silver nitrate solution for one minute, drained, and then baked at 105C for 4 hours. The heated iodine entering the column combines chemically with the silver and is retained on the column. The chemistry of this process is complex. Entering gases contain NO₂, O₂, H₂O, N₂ and I₂. The following reactions probably take place:

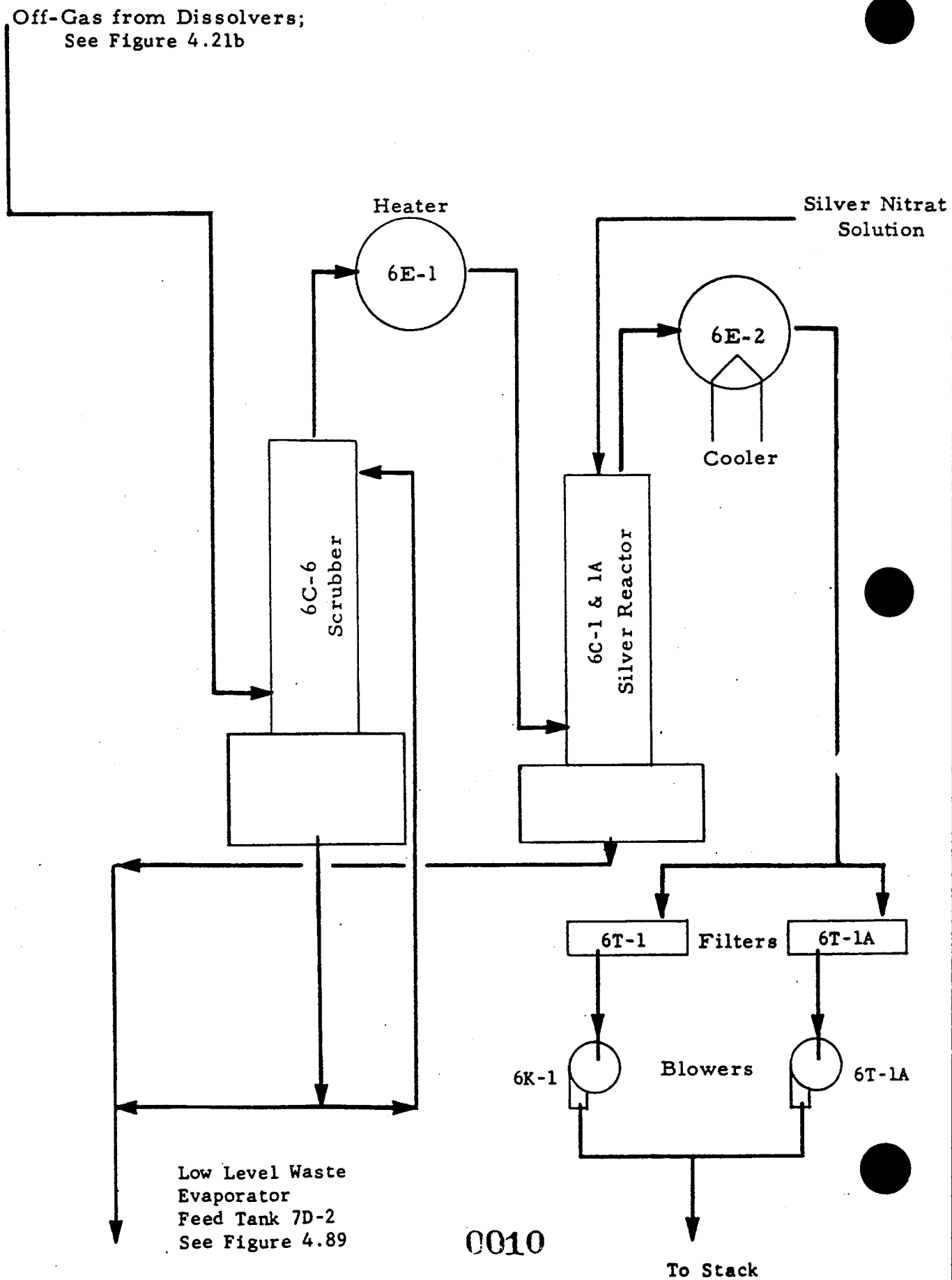


High collection efficiencies are favored by high temperatures but the temperature must be kept below 212 C lest the silver nitrate melt and run off the packing. At temperatures below 110 C essentially no iodine removal occurs. Radioactive xenon and krypton are diluted to safe limits with plant ventilation air and by stack diffusion.

4.28 Silver reactors have been operated for periods up to a year with iodine removals of 99.99 per cent. The more generally expected figure is about 99.5 per cent. When the efficiency of a unit begins to fall (indicated by a rise in the stack gas monitor reading), it can be regenerated by cooling the reactor to 65 C and spraying the packing with 0.04 cubic feet of 5 M silver nitrate per cubic foot of packing. The bed is then heated to 105 C and baked for 4 hours. This process is then repeated with the baking done at 110 C for six hours. Regeneration produces a liquid waste which is sent to the tank farm via the general purpose evaporator (ARC 7C-5).

Revision 1, October 29, 1962
Revision 2, May 30, 1964

Figure 4.26
Treatment of Dissolver Off-Gases



0010

4.29 When the dissolution of the fuel in the dissolver is complete the solution is cooled to 90 to 100 F and jetted to the accountability and feed adjustment tank (CPC-3D-1). Rinse acid is added through sprays in the dissolver barrels. This is jetted to the feed adjustment tank also. The hulls are then returned to the GPC by the reverse mechanism whereby the chopped fuel was introduced into the dissolver. The handling of the hulls was described in Paragraph 4.18 through 4.20. The dissolver is now ready to take another charge.

4.30 Mixed thorium-uranium oxide fuels such as the Indian Point Core A are dissolved in a concentrated nitric acid solution containing 0.04 M NaF and 0.075 M boric acid. The fluoride ion is added to promote the dissolution of the ThO_2 - UO_2 fuel which is not readily dissolved by concentrated nitric acid alone. The boric acid is added as a neutron poison for criticality control. The dissolution time for fuel of this type is expected to be 24 to 48 hours. At the completion of dissolution the concentration of thorium, uranium and nitric acid in the solution will be 238 and 17 grams per liter and 8.8 M respectively. In order to prepare a suitable feed for solvent extraction the nitric acid concentration is reduced to 4.4M by addition of rinse water, which also proportionally reduces the concentration of all other ions.

4.31 Highly enriched (25% initial) uranium-molybdenum alloy fuels which are clad in zirconium, such as Fermi Core A, will dissolve in nitric acid with ferric ion added to stabilize the molybdenum in solution but the enrichment of the uranium and/or molybdenum content determines the concentration of uranium permissible in the feed. In the case of Fermi Core A, the maximum concentration of uranium permitted in the dissolver solution for criticality reasons will be 20 grams per liter of total uranium or 5 grams per liter of U-235. At the above concentration of uranium, the molybdenum concentration is such that precipitation of uranium-molybdenum complex in the presence of ferric ion does not occur, therefore, only nitric acid (4.0M) containing 1 gram per liter $\text{Fe}(\text{NO}_3)_3$ is required as the dissolvent and the volume of dissolution reagent added to the dissolver will be adjusted to provide for a terminal concentration of uranium of no greater than 20 grams per liter.

4.32 Low enriched uranium-molybdenum alloy fuels containing 3 per cent or less molybdenum, such as Piqua fuels, will be processed in a similar manner. However the terminal concentration of uranium in solution will be restricted to such a value that the solubility of molybdenum in the solution is not exceeded when small quantities of ferric ion are present. For fuels of this type, the uranium concentration in dissolver solution will not exceed 150 grams/liter and again this terminal concentration will be achieved by adding the proper volume of dissolution reagent. The Piqua fuel is clad with 0.035 inches of aluminum. This cladding is removed by adding 5.3M NaNO_3 6.9 M NaOH to the dissolver. The NaOH dissolves the jacket forming NaAlO_2 and the NaNO_3 suppresses the hydrogen evolved. The solution is heated to boiling for one hour or

until the reaction subsides, then the solution is cooled and jetted to the low level waste evaporator feed tank (7D-2). The fuel is then rinsed with water with this rinse also going to the low level waste evaporator feed tank. Dissolvent is then added and dissolution proceeds as with the other fuels. The beds in the silver reactors are by-passed during de-jacketing to prevent the traces of NH_3 generated from displacing the active iodine.

4.33 Alloy Fuels. The alloy fuels are not sheared but are placed in the dissolver baskets directly. They are brought in from Fuel Receiving and Storage to the PMC in the same manner as the other fuels. End fittings and other extraneous metal are removed by sawing or other means in the PMC. The fuel bearing portion is then transported directly with the bridge crane to the GPC hatch. Fuel is lowered into the GPC directly into a fuel basket through this hatch using the bridge crane. The fuel baskets are then placed in the dissolvers in the normal way.

4.33a Zirconium-uranium Fuel. Zirconium-uranium alloy fuels are dissolved by the Niflex process. The fuel is charged to the dissolvers and nitric acid is added at a concentration of 1 M. The solution is sparged with nitrogen to dilute the off-gases which contain hydrogen. After the solution has been heated to 90 C, 27 M HF is metered into the dissolver at a rate of $\frac{1}{2}$ gal/min. At the completion of the dissolution $\text{Al}(\text{NO}_3)_3$ is added to complex the excess fluoride ion and the solution digested for 30 minutes. The solution is then cooled to 40 to 50 C and jetted to the feed adjustment tank.

4.33b MTR-Aluminum-Uranium Alloy Fuels. Aluminum-uranium alloy is dissolved in 5.4 M nitric acid. The dissolution is catalyzed with 0.005 M mercuric nitrate. The acid and catalyst are charged together into the dissolver cold. With the dissolvent in, the dissolver contents are heated to initiate the reaction. Once started the reaction proceeds rapidly and the dissolver contents must be cooled to keep the off-gas rates within acceptable limits.

When the reaction begins to subside, the dissolver contents are again heated up to the boiling point and refluxed until the reaction is complete. Contents are then cooled and jetted to the feed adjustment tank.

Feed Adjustment

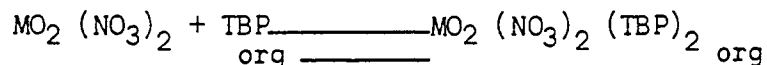
4.34 Dissolver solution and rinses are collected in the accountability and feed adjustment tank (CPC-3D-1). This is a 304-L stainless steel tank equipped with heating and cooling coils, condenser, air sparger, liquid level and specific gravity instruments and is vented through the feed adjustment condenser (CPC-3E-1). Cold chemicals may be added to this tank directly from the extraction cold chemical area. Contents of this tank are sparged and sampled. This sample serves as an accountability sample, the tank contents are evaporated or butted with cold chemicals to bring into feed specifications. After adjustment the tank contents are cooled, if

necessary, and jetted to the partition cycle feed tank (XCI-4D-1). Concentrates from the rework evaporator (see Paragraph 4.95) can be added to (CPC-3D-1) when re-cycle is necessary.

Solvent Extraction--Partition Cycle

4.35 The feed in the partition cycle feed tank (XC1-4D-1) is now ready for introduction into the battery of solvent extraction columns all of which are located in the first three of the contact-maintained cells (XC1, XC2, XC3). The base-line fuel is put first through a partition cycle which separates out the bulk of the fission products into an aqueous waste stream and splits the uranium and plutonium into two separate partially decontaminated aqueous product streams. The two product streams are then separately subjected to additional solvent extraction cycle and final cleanup steps. A schematic flowsheet of the partition cycle is shown in Figure 4.35. A detailed description of the columns and their appurtenant equipment and instrumentation is given in Section V.

4.36 The extraction of metal ions from nitric acid solutions by TBP is due to the formation of metal nitrate-TBP complexes which are preferentially extracted into the organic phase. The complexes are neutral and are not dissociated significantly in the organic solvent. These complexes are of the forms $M(IV)(NO_3)_4(TBP)_2$ and $MO_2(TBP)_2$ formed from tetravalent and the so-called "yl" ions respectively. The extraction of the metal ions into the organic phase can be considered a complex formation between the neutral complex $MO_2(NO_3)_2$, present in the aqueous phase, and two molecules of TBP:



Ions other than the tetravalent and "yl" types give only weak nitrate-TBP complexes. In solutions of irradiated fuel, the actinides are principally present as "yl" and tetravalent ions; most of the fission products form ions of a lower charge. Therefore, the TBP extraction effectively separates uranium and plutonium from the fission products.

4.37 There is one fission product, zirconium which is capable of forming a tetravalent ion, but the extraction of Zr^{+4} is considerably hindered by its hydrolysis which persists even in solutions of quite high acidity. Nevertheless, Zr (IV) always poses a problem in obtaining complete decontamination. The same is true of ruthenium which exhibits an especially capricious behavior, since the amount of extractable ruthenium is highly dependent on the previous treatment of the solution. It is these two fission products which account for most of the activity in the later steps in the process.

Revision 1, October 29, 1962
Revision 2, May 30, 1964

4.38 The stripping step is essentially the reverse of the extraction; i.e., the equation given in Paragraph 4.36 must proceed as far to the left as possible. This is accomplished by keeping the nitrate ion as low as possible. Pure water is, therefore, a good stripping agent but in order to promote phase separation it is desirable to use a dilute solution of nitric acid; e.g., 0.01 M.

4.39 In the partitioning of uranium and plutonium advantage is taken of two facts:

1. Actinide (III) ions are extracted only slightly by TBP, even at nitrate concentrations where such elements in the tetra- and hexavalent states would be extracted extensively.
2. Pu (IV) is easily reduced to Pu (III) at redox potentials where uranium still stays hexavalent. For instance, Pu (IV) is reduced to Pu (III) by Fe added as ferrous sulfamate; whereas U (IV) is not reduced.

The reduction of Pu (IV) is rapid and may be accomplished by adding the ferrous sulfamate to the scrub solution in the partitioning column.

4.40 To carry out the partition cycle in the plant, the feed solution is pumped into the partition cycle extraction column (HA; XC1-4C-1) by use of an air pump or an airlift (XC1-4J-1A, -1B). Other influent streams to this column include a nitric acid scrub stream (HAS) introduced at the top of the column and the kerosene-tributyl phosphate solvent (HAX) introduced at the bottom. Since this stream may use recovered solvent, it is fed from either the first or second cycle solvent storage tanks (XC2-13D-4, -5). The pumps for this stream (13G-11, -11A) are located in shielded niches in the Lower Warm Equipment Aisle. In common with all the columns, the fluids contained herein are pulsed using an air pulser located on top of the extraction cells.

4.41 Greater than 99.5 per cent of the uranium and plutonium are taken overhead with the organic product stream (HAP). This stream is put through a disengaging section to allow entrained aqueous phase to separate out, mixed with the organic waste stream from the plutonium cycle (IIBW) and pumped into the plutonium partitioning column (HB). The waste stream (HAW), containing greater than 99.9 per cent of the fission products is collected in the partition cycle waste catch/hold tank (XC1-4D-2). This is a bicylindrical tank. When the one portion of the tank is full the solution is jetted into the other portion in which it is mixed, sampled, and held for determination of the analyses before being sent on to acid recovery and waste storage or to product rework.

4.42 The HAP stream is fed into the bottom of the partition column (XC1-4C-2). This is joined by an organic stream from the top of the Pu scrub column and by the solvent waste from the plutonium cycle (IIBW). All are pumped in by one of two pumps (LWA 4G-5, -5A). A reducing aqueous strip stream (HBX) is introduced at the top of the column. This is a cold stream pumped from the solution make-up area and contains the reductant ferrous sulfamate. The plutonium is reduced to the (III) valence state in which the distribution ratio highly favors the aqueous phase. There is sufficient nitric acid in the system, however, to keep the uranium in the solvent phase so that it goes essentially quantitatively overhead with the organic product stream (HBU). The plutonium is removed from the bottom of the column in an aqueous stream which is then put into the top of the plutonium scrub column (XC1-4C-3).

4.43 The function of the plutonium scrub column is to effect complete separation of the uranium and plutonium. The organic scrub stream is drawn from tank 13D-4, located in Cell #2. The plutonium product stream (HBP) is drawn from the bottom of this column and collected in the plutonium feed conditioner (4D-6) from whence it is sent to the plutonium cycle where it is further purified.

4.44 In the uranium strip column (HC; XC2-4C-4) the HBU stream is heated to 140F and introduced into the bottom of the column with pumps WEA-4G-9, -9A). A strip solution (HCX) consisting of 0.01 M HNO_3 is pumped into the top of the column from the solution make-up area. This stream is also heated to 140 F. In this column the nitric acid concentration is low enough so that the uranium is re-extracted into the aqueous phase and removed from the bottom of the column in the HCU stream. This is collected in a feed conditioner tank (XC2-4D-9) wherein it is sampled and becomes feed for the first uranium solvent extraction cycle. A solvent waste stream (HCW) is taken overhead from the column and sent to the first set of solvent washing equipment.

4.45 The first core of the Indian Point reactor contains a fuel made from mixed thorium-uranium oxides. It was originally planned to process this fuel to recover both the uranium and the thorium. Since there is going to be only one of this type of core, the thorium recovery equipment will not be included. The thorium and fission products will go out together in the HAW stream. This stream will be evaporated to concentrate the thorium and to remove as much free nitric acid as possible. Bottoms from the evaporator will be removed when the thorium concentration reaches 450 g/liter. The waste will then be partially neutralized to reduce the free nitric acid concentration. After partial neutralization the waste will be transferred to a stainless steel waste tank for storage. The waste tank is provided with cooling coils and the temperature of the waste solution will be maintained at 55-60 C.

Revision 1, October 29, 1962
Revision 2, May 30, 1964

4.46 Mixed thorium-uranium feed (see Paragraph 4.30) is pumped from the partition cycle feed tank (XC1-4D-1) into the extraction section of the partition cycle extraction column (HA; XC1-4C-1) by use of the same feed pumps used for the base-line fuels. Other influent streams to this column include a nitric acid scrub stream (HAS) introduced at the top of the column and the kerosene-TBP solvent (HAX) introduced at the bottom. In this case the concentration of TBP in the solvent is only 5% rather than the normal 30% to limit the concentration of the enriched uranium in the overhead solvent (and subsequent streams) to less than five grams per liter.

4.47 Greater than 99.5 per cent of the uranium is taken overhead with the organic product stream (HAP). This is put through a disengaging section to allow entrained aqueous phase to separate out. Even though the amount of plutonium in this fuel is negligible, the HAP stream is still introduced into the partition column wherein it is effectively scrubbed with both an aqueous and an organic scrub stream. This serves to remove the last traces of thorium from the uranium. The stream coming off the bottom of the scrub column (XC1-4C-3) would normally be the plutonium product stream. In this case it is an aqueous waste stream containing the residual thorium. It is collected in the plutonium cycle feed conditioner (XC2-4D-6). In order not to cross-connect product and waste tanks, this stream is allowed to flow through its normal channels. This means that this waste stream will be introduced into the plutonium extraction column (IIA). It is allowed to flow down through this non-operating column and is collected in the IIAW waste catch tank from which it is sent to acid recovery and waste storage. The uranium, scrubbed in the two partition columns, is introduced into the bottom of the strip column (XC2-4C-4) as with the base-line fuels and is taken into an aqueous product stream and collected in the first uranium cycle feed conditioner (XC2-4D-9) after which it is treated just like the base-line fuels except that the TBP concentration of the solvent is 5% throughout.

4.48 The waste stream (HAW) is flowed via a level controller and head pot into the partition cycle waste catch/hold tank (XC1-4D-2) and is treated the same as the base-line waste except that after neutralization it is stored in a separate cooled tank.

4.49 Highly enriched uranium-molybdenum alloys used in Fermi Core A (see Paragraph 4.31) are processed in the same equipment as the base-line fuels and Figure 4.35 applies. However, the TBP concentration in the solvent is cut to 10% to limit the concentration of uranium in the organic phase for criticality reasons. Low-enriched uranium-molybdenum alloys (see Paragraph 4.32) are processed in a manner similar to the base-line fuels as are the SCRUP fuels.

Revision 1, October 29, 1962
Revision 2, May 30, 1964

4.50 Uranium-zirconium alloy fuels are dissolved as discussed in Paragraph 4.33a and are processed through the extraction equipment much as described for the main line fuels. There is a small quantity of plutonium in these fuels, however; the Pu-240 content is high and it is not worth recovering. Partitioning is done in the HBX column with the HBP stream from this column routed to the low level waste and acid recovery via the IIA column. The IIA column is not operated as a column in this instance but merely serves as a path in the routing of the HBP stream. The second and third uranium cycles operate the same high enriched evaporator and uranium packaging. A 5% TBP solvent is used throughout for these fuels.

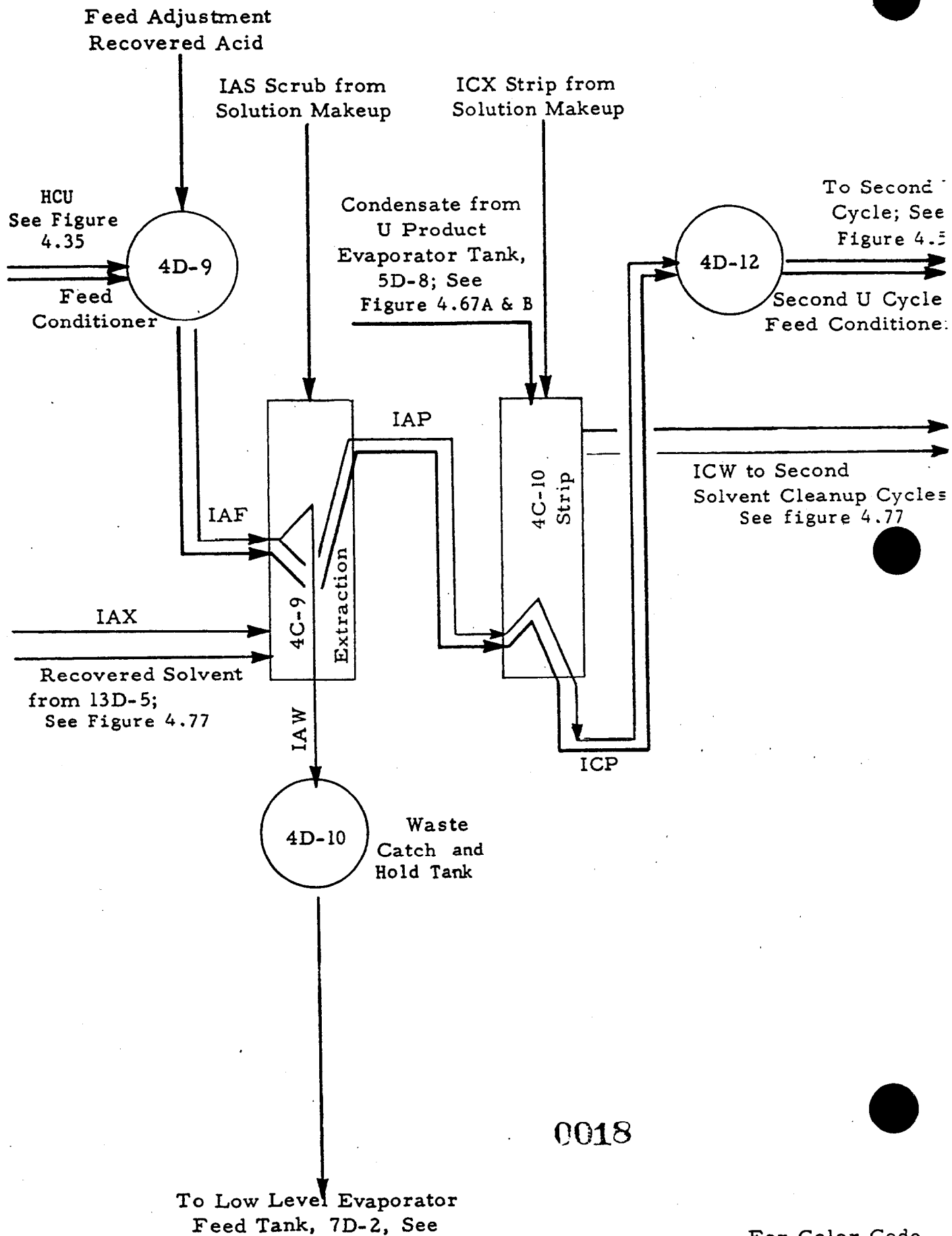
4.51 Uranium-aluminum alloy fuels are dissolved as discussed in Paragraph 4.33b and are routed through the processes as described in Paragraph 4.50. Again a 5% TBP solvent is used for these fuels.

4.52 The first uranium cycle is provided for additional decontamination of uranium from fission products and plutonium. The uranium product stream from the partition cycle (HCU) flows continuously into a feed conditioner (XC2-4D-9) where concentrated nitric acid is added at a metered rate to provide the salting required for re-extraction. The feed conditioner will be sampled occasionally to determine if feed specifications are being maintained; however, primary control will be by instrument. The first uranium cycle consists of a pair of pulsed columns. In the first column the uranium is re-extracted into the organic phase leaving behind fission products and residual plutonium in the aqueous phase. The uranium in the organic phase is then back-extracted into the aqueous phase in the second column. A schematic representation of the first uranium cycle is shown in Figure 4.52.

4.53 The feed solution is then introduced into the extraction section of the first uranium cycle extraction column (XC2-4C-9) by air lifting the solution into a head pot and allowing it to flow into the column. Other influent streams to this column include two nitric acid scrub streams (1AS, 1AS') which are pumped into the top and upper sections of the column from the solution make-up area or from the recovered acid storage tank (SST-7D-5); and the kerosene-TBP solvent (1AX) pumped (LWA-13G-12) into the bottom of the column through a head pot. Recovered solvent from tank XC2-13D-5 is used.

Figure 4.52

Schematic of First U Cycle



0018

4.54 Greater than 99.5 per cent of the uranium is taken overhead with the organic product stream (1AP). This stream is put through a disengaging section to allow entrained aqueous phase to separate out, heated to 140 F and then introduced into the bottom of the strip column with pumps LWA-4G-23, -26A. The aqueous waste stream (1AW), containing about 95 per cent of the fission products entering with the feed to this cycle, is collected in the first uranium cycle waste catch/hold tank (LWC-4D-10), a bicylindrical tank. When one portion of the tank is full the solution is jetted into the other portion in which it is mixed, sampled, and held for analyses before being sent on to acid recovery and waste storage or to product rework.

4.55 In the uranium strip column (XC3-4C-10) the 1AP stream introduced at the bottom of the column is contacted with a strip solution consisting of 0.01 M HNO_3 which is pumped into the top of the product evaporator condensate tank (PPC-5D-8; See Figure 4.67 A and B) is also added to this stream. In this column the uranium is transferred into the aqueous phase and removed from the bottom of the column in the ICP stream. This is collected in the second uranium cycle feed conditioner (XC3-4D-12) wherein it is sampled and feed for the second uranium cycle is prepared. A solvent waste stream (1CW) is taken overhead from the column and sent to the second cycle solvent cleanup system.

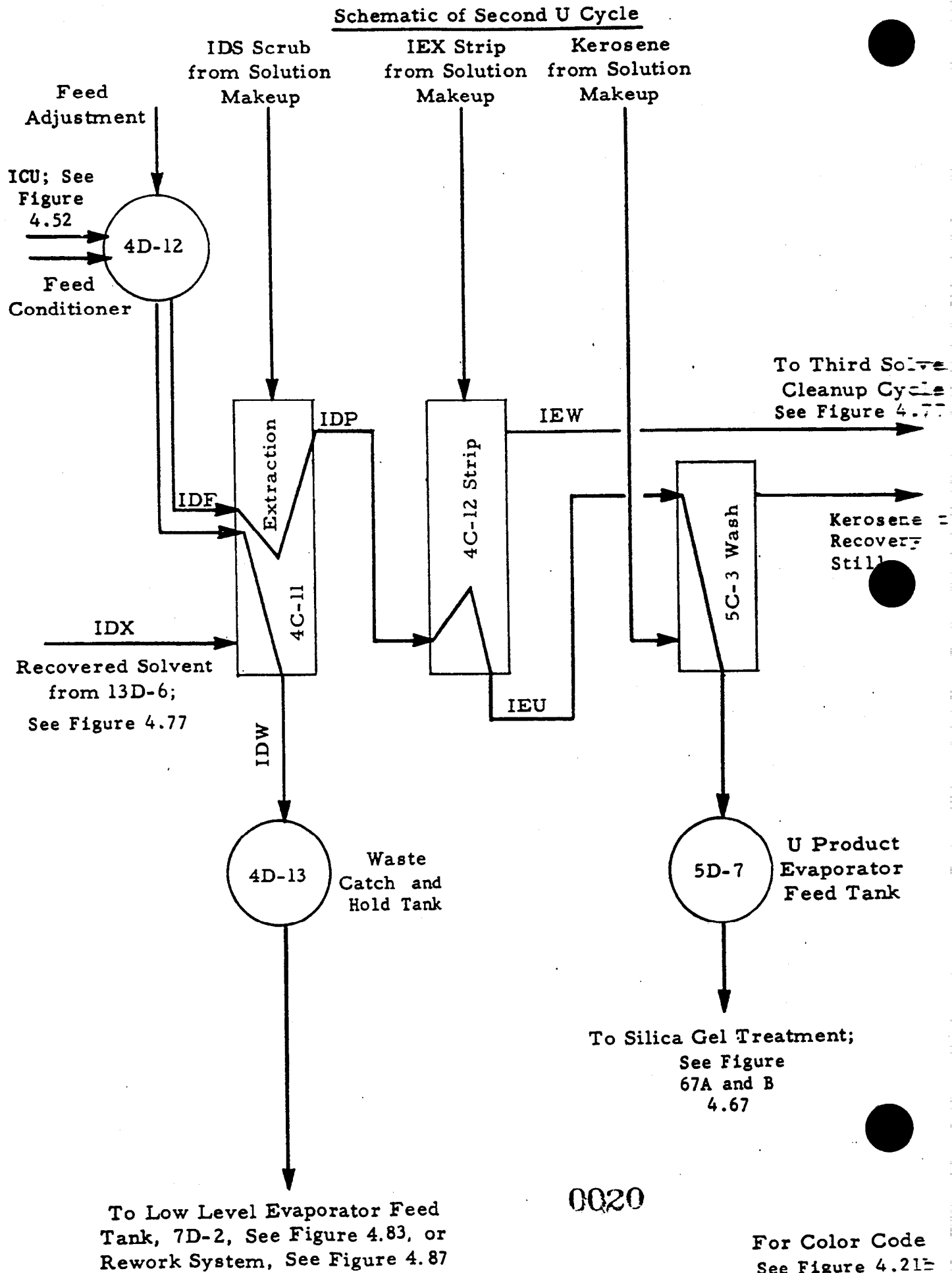
4.56 All of the fuels are processed through the first uranium cycle in the same equipment and Figure 4.52 applies to all of them. However, for the enriched fuels, the TBP concentration in the solvent is reduced to 10% or 5% for criticality control.

Solvent Extraction--Second Uranium Cycle

4.57 The uranium product stream from the first uranium cycle (ICU) is collected in the feed conditioner tank (XC3-4D-12). After sampling, analyses, and adjustment of acid concentration, this stream is ready for additional decontamination which is carried out in a manner completely analogous to the first uranium cycle. This operation is called the second uranium cycle. A schematic representation of this cycle is shown in Figure 4.57. As in the partition and first uranium cycles, the uranium is extracted into an organic phase in the first column leaving most of the fission products in the aqueous phase. In the second column the uranium is taken back into an aqueous product stream.

4.58 The feed solution is then introduced into the extraction section of the second uranium extraction column (XC3-4C-11) by air lifting it into a head pot and allowing it to flow into the column. Other influent

Figure 4.57



streams to this column include two nitric acid scrub streams (1DS, 1DS') which are pumped into the top and upper section of the column from the solution make-up area; and the kerosene-TBP solvent (1DX) pumped (LWA-13G-13) into the bottom of the column from the No. 3 solvent storage tank (XC3-13D-6).

4.59 Greater than 99.5 per cent of the uranium is taken overhead with the organic product stream (1DP). This stream is put through a disengaging section to allow entrained aqueous phase to separate out, heated to 140 F and then introduced into the bottom of column (XC3-4C-12) with pumps LWA-4G-31, -31A. The aqueous waste stream (1DW), containing about 90 per cent of the fission products entering with the feed to this cycle, is collected in the second uranium cycle waste catch/hold tank (LWC-4D-13), a bicylindrical tank. When one portion of the tank is full the solution is jetted into the other portion in which it is mixed, sampled, and held for analyses before being sent on to acid recovery and waste storage or to product recovery.

4.60 In the uranium strip column (XC3-4C-12) the 1DP stream introduced at the bottom of the column is contacted with a strip solution consisting of 0.01 M HNO_3 which is pumped into the top of the column from the solution make-up area. In this column the uranium is transferred into the aqueous phase and removed from the bottom of the column in the 1EU stream. The organic stream 1DW is routed to the third cycle solvent wash system.

4.61 The uranium product stream (1EU) is collected in the uranium product evaporator feed tank (PPC-5D-7), a stainless steel tank filled with boron-glass Raschig rings.

4.62 All of the fuels are processed through the second uranium cycle in the same equipment, and Figure 4.57 applies to all of them. However, for the enriched fuels the TBP concentration in the solvent is reduced to 10% and 5% for criticality control.

Solvent Extraction Column--Plutonium Cycle

4.63 The plutonium product stream from the partition cycle (HBP) is collected in the plutonium cycle feed conditioner tank (XC2-4D-6) as explained in Paragraph 4.42. In this tank the acid concentration is adjusted and sodium nitrite is added to reoxidize the plutonium to the Pu (IV) state so that it may be re-extracted into an organic solvent. Waste from the plutonium ion exchange treatment is recycled to this tank. Just as the uranium product stream is put through additional solvent extraction cycles, so the plutonium is likewise treated, although in the case of plutonium only a single additional solvent extraction cycle is used since

the subsequent concentration of the plutonium product by ion exchange (see Paragraph 4.74 through 4.76) provides additional decontamination. A schematic representation of the plutonium solvent extraction cycle is shown in Figure 4.63. As in the partition cycle, the plutonium is extracted into an organic phase in the first column leaving most of the fission products in the aqueous phase. In the second column the plutonium is stripped into an aqueous product stream.

4.64 The feed solution is introduced into the extraction section of the plutonium cycle extraction column (XC2-4C-7) by pumping it into a head pot and allowing it to flow into the column. Other influent streams to this column include a nitric acid scrub stream (IIAS) which is pumped into the top of the column from the solution make-up area; and the kerosene-TBP solvent (IIAX) pumped through a head pot by pumps (LWA-13G-11, -11A; LWA-13G-12).

4.65 Greater than 99.5 per cent of the plutonium is taken overhead with the organic product stream (IIAP). This stream flows from the top of the extraction column to an intermediate point in the strip column. The aqueous waste stream (IIAW), containing about 95% of the fission products entering with the feed to this cycle, is collected in the plutonium cycle waste catch/hold tank (LWC-4D-8) a bi-cylindrical tank. When one portion of the tank is full, the solution is jetted into the other wherein it is mixed, sampled, and held for analyses before being sent to waste treatment or to rework.

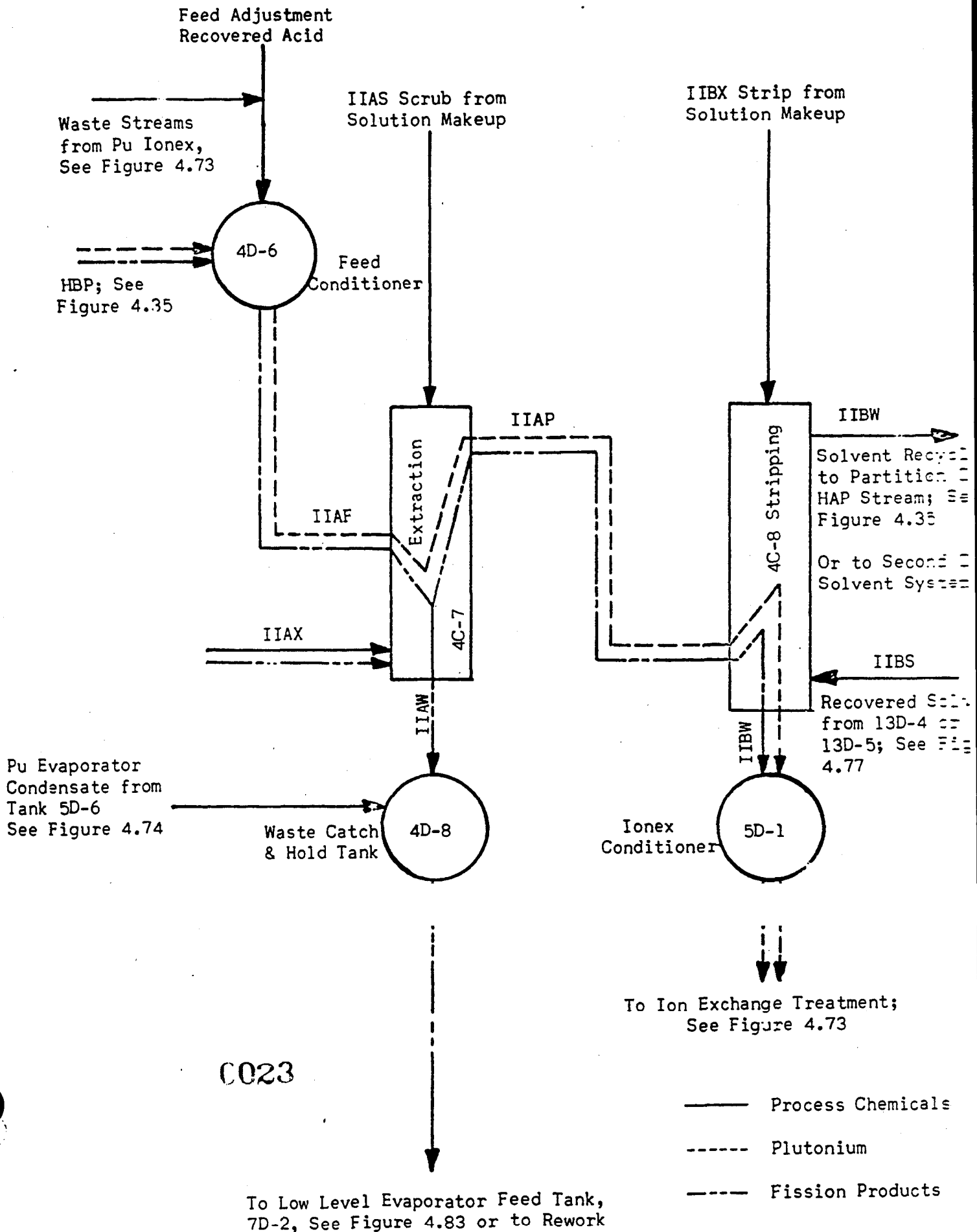
4.66 In the plutonium strip column (XC2-4C-8) the IIAP stream is introduced into an intermediate point and is contacted with a strip solution (IIBX) which is pumped into the top of the column from the solution make-up area and with an organic scrub stream (IIBS) which is pumped into the bottom of the column through a head pot by means of pumps (LWA-13G-11, -11A; LWA-13G-12). In this column the plutonium is transferred back into the aqueous phase and removed from the bottom of the column in the IIBP stream. This is collected in the ion exchange conditioner tank (XC3-5D-1). A solvent waste stream (IIBW) taken overhead from the column is pumped back into the partition cycle by joining it with the HAP stream (see Paragraph 4.42).

Product Purification and Concentration

4.67 The uranium product stream from the second uranium cycle (IEU) is collected in the uranium product evaporator feed tank (PPC-5D-7)

Rev. 4, September 1969

Figure 4.63
Schematic of Plutonium Cycle



as indicated in Paragraph 4.61. For highly enriched fuels this solution is fed directly to the silica gel beds (see Paragraph 4.70). For low-enriched fuels this solution is concentrated before being passed through the silica gel beds. Two evaporators are provided, one for low-enriched fuels, the other for fully enriched fuels. The routing of the low enriched uranium through evaporation and silica gel decontamination is shown in Figure 4.67A. Figure 4.67B shows the routing for the high enriched uranium. The low enriched uranium product is air-lifted to evaporator (PPC-5C-4). It is made of 304-L stainless steel and is of such a size and contains sufficient fixed poison that it is critically safe for all concentrations of uranium. Evaporator (PPC-5C-5) is used for fully enriched fuels. This evaporator is also made of 304-L stainless steel; it is sized to be geometrically safe under all conditions. Both evaporators are described in more detail in Section V.

4.68 Condensate from either evaporator is collected in the uranium product evaporator condensate tank (PPC-5D-8). This is a stainless steel tank containing boron-glass Raschig rings. The condensate is returned to the first uranium cycle strip column by pumps UWA-5G-1, -1A. Concentrate from the low-enriched evaporator is collected in the uranium product surge tank (PPC-5D-9). This is a stainless steel tank containing boron-glass Raschig rings. From here the concentrated product is pumped to the silica gel columns using pumps LWA-5G-2, -2A. Concentrate from the highly enriched evaporator (the Feed to which has already been through the silica gel columns) goes directly to highly enriched product storage.

4.69 The purpose of the silica gel treatment is to decontaminate the uranium solution from the last traces of zirconium and niobium. Silica gel is a very selective absorber for these fission products, and does not absorb uranium. The uranium product solution containing about 0.1 M HNO_3 is passed through silica gel beds. Under these conditions the uranium passes through the column unadsorbed while zirconium and niobium are taken up on the column along with any remaining plutonium. The sorption rate of Zr-Nb is slow so columns with long hold-up times are required. Regeneration of the columns is accomplished in two steps. First the column is washed with 0.25 M HNO_3 to rinse the column free of uranium. Regeneration is then accomplished with 0.4 M oxalic acid solution. A schematic flowsheet for the silica gel treatment is included in Figures 4.67A, and B.

4.70 The low enriched uranium product from Tank 5D-9 (PPC) is pumped into the silica gel columns (PPC-5C-6A, 6B) by pumps (LWA-5G-2, -2A). These columns are 10 inches in diameter by 12.5 feet long. The uranium product flows down through the column and is not absorbed by the silica gel. The product comes out the bottom of the column essentially decontaminated from the last of the fission products and is collected in the

Revision 1, October 29, 1962
Revision 2, May 30, 1964

Figure 4.67A
Low Enriched U Product
Evaporation and Final Decamination
Schematic

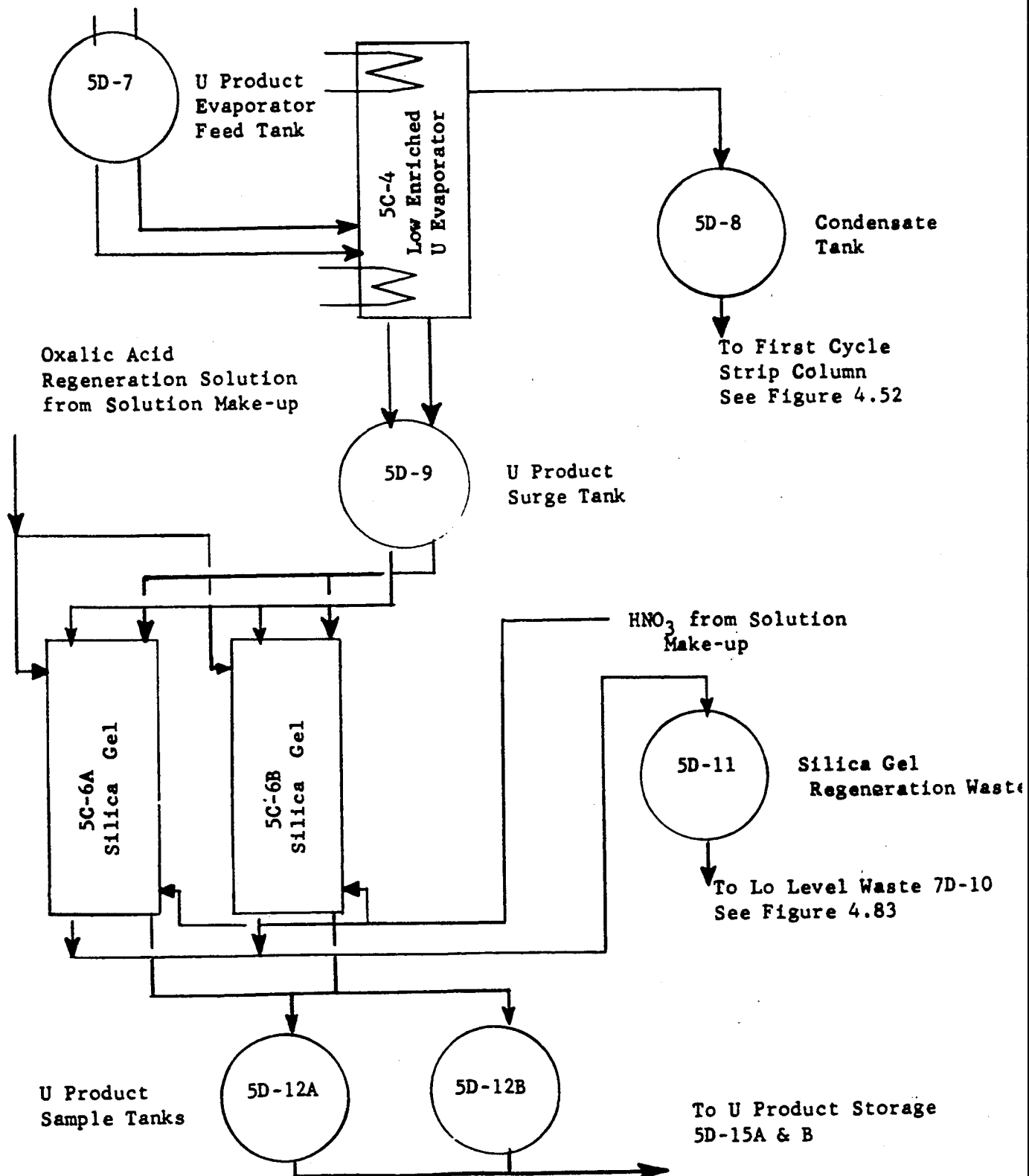
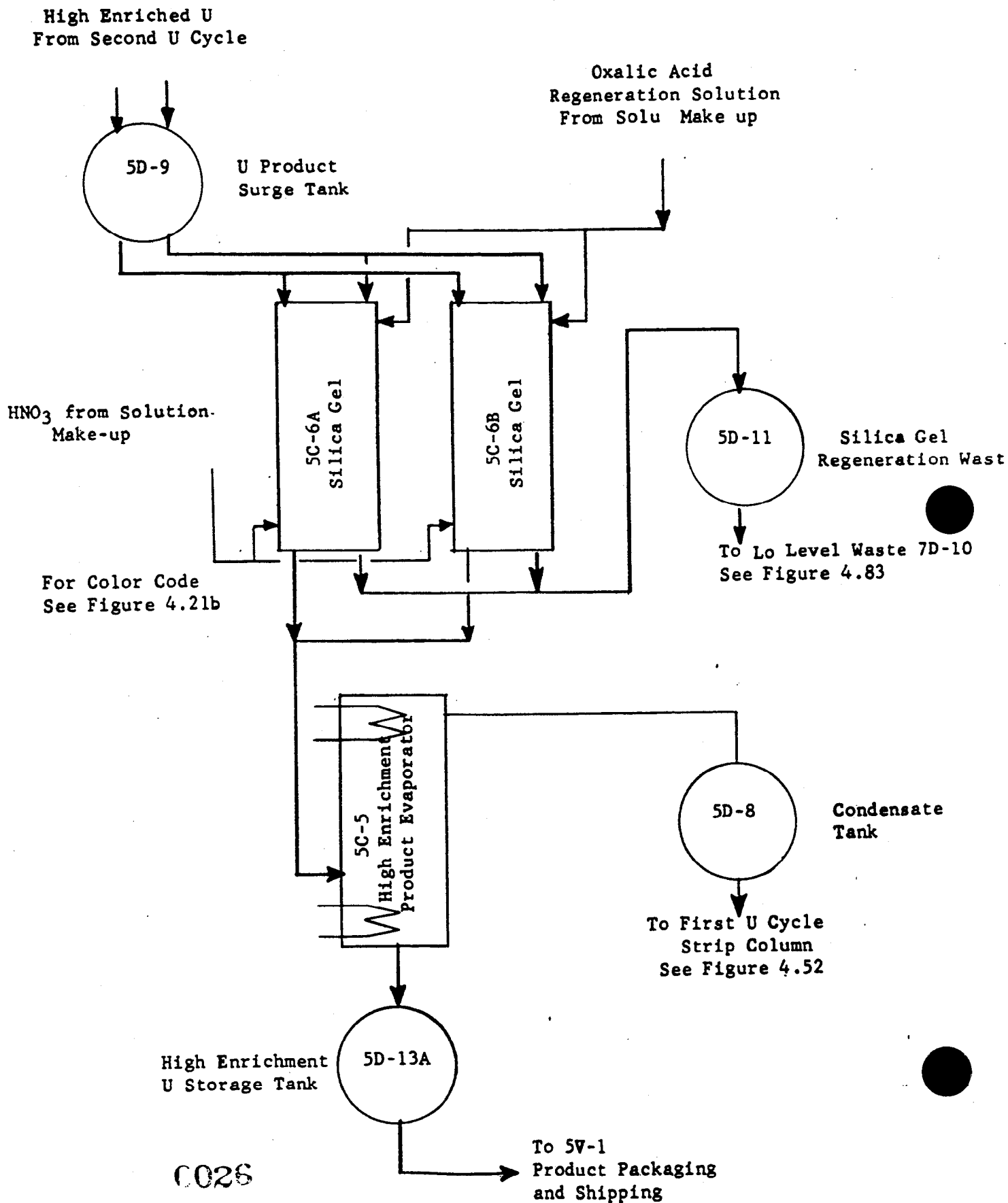


Figure 4.67b
High Enriched U Product
Final Decantamination and Evaporation
Schematic



product sampling tank (PPC-5D-12A, 5D-12B). After sampling and analyses, the product is transferred to one of two product storage tanks (PPC-5D-15A1-15B). If the product does not meet specifications the solution can be routed to an off-specification tank (5D-15A2) for recycling. The highly enriched uranium product is pumped from tank 5D-9 to the silica gel column before evaporation. From the silica gel column the product solution is routed to the high enriched uranium evaporator (PPC-5C-5). After evaporation, the concentrated product is let down to the high enriched evaporator surge tank 5D-13A. From this tank the product solution is routed to 5D-13B for storage. Tanks 5D-13A and B contain sufficient fixed poison to be critically safe even under abnormal plant conditions.

4.71 After a number of batches of product have gone through the silica gel columns, it is necessary to regenerate them. This is done by first rinsing the columns with a small amount of 0.25 M HNO_3 introduced into the top of the columns from the solution make-up area. This will remove uranium from the columns. This rinse is added to the product solution. The columns are next eluted with 0.4 M oxalic acid at 80-90 C which is pumped into the bottom of the columns from the solution make-up area. This removes the zirconium and niobium from the columns. The waste stream is collected from the column in regeneration waste tank (PPC-5D-11), stainless steel tank containing boron-glass Raschig rings. The regenerant solution is sent to waste storage via tank (7D-10). Residual oxalic acid is removed from the bed with a demineralized water flush.

4.72 The high enriched uranium product is collected and stored as uranyl nitrate solution in stainless steel tanks containing sufficient fixed poison that they are critically safe even under abnormal plant conditions. A list of these tanks is given in Section V. Low-enriched uranium product solution is collected batch wise in either PPC-5D-12A or PPC-5D-12B. At this point samples are taken to determine that the product meet chemical specifications for recovered uranium. If it does meet the specifications, the product is transferred to storage tanks (UPC-5D-15A; PPS-5D-15B). For shipment the low-enriched product solution is transferred batch wise from the storage tanks by pump (PPS-5G-6) to weight tank (PPS-5V-1) for weighing and accountability. Finally the product solution is transferred from the weight tank to a tank truck for return to the customer. In the case of the highly enriched product solution, the dilute solution from the silica gel columns is concentrated to 175 to 225 g/l in evaporator (PPC-5C-5) and collected batch wise in tanks (PPC-5D-13A and -13B). These tanks contain sufficient fixed poison that they are critically safe. From here the solution will be pumped in small batches to measuring tank (PPS-5Y-21), a geometrically safe tank, and from there will be drawn into geometrically safe shipping containers.

4.73 The Plutonium product stream from the Plutonium cycle (IIBP) is collected in the ion exchange feed conditioner tank (XC3-5D-1) as indicated in Paragraph 4.66. Acid is added to make the nitric acid concentration 7.2 M. This solution is then loaded onto one of three anion exchange columns (PPC-5C-1A, 1B, 1C) at 60 C, the optimum temperature for sorption. Plutonium is absorbed strongly, but fission products and uranium go on through in the waste which, because it may contain some small quantity of plutonium, is recycled to the feed conditioner (XC2-4D-6) for the plutonium extraction cycle. After the plutonium has been loaded onto the resin column, it is washed with 7.2 M nitric solution to remove the residual fission products and finally eluted using 0.6 M nitric acid. The product stream from the elution step is collected in the geometrically safe slab plutonium product evaporator feed tank (PPC-5D-4) from which it is pumped to the plutonium evaporator for concentration. After elution the resin column is washed with 7.2 M nitric acid. The regeneration solution along with the wash solution is recycled to solvent extraction. A schematic flowsheet of the ion exchange treatment of the plutonium is shown in Figure 4.73.

4.74 The Plutonium product stream from 5D-4 is next evaporated. A schematic flowsheet for this step is given in Figure 4.74. The product is fed into the geometrically safe plutonium evaporator (PPC-5C-2), a titanium vessel. Overheads from the evaporator are collected in an evaporator condensate tank (PPC-5D-6), a stainless steel tank containing boron-glass Raschig rings. From here the condensate is transferred to either tank 4D-8 or 5D-4 for evaporation or recycling. The vaporator concentrate is collected in one of two plutonium product storage tanks (PPC-5D-5A, 5B), 2.5 inch wide slab tanks wherein the product is sampled and from which it is transferred to product packaging and shipping.

4.75 The plutonium packaging equipment is enclosed in a ventilated glove box. The product is then transferred from the measuring tank (5D-17) to a product shipping container which is stored in a bird cage until a shipment is ready. All equipment used is geometrically safe for credible concentrations.

Solvent Recovery

4.76 The reuse of solvent is an economic necessity in solvent extraction processes. Because the kerosene-TBP solvent picks up certain of the fission products and because radiolytic decomposition products of the solvent, particularly di-n-butyl phosphoric acid (DBP), increase this effect and reduce the decontaminating power of the solvent, it is necessary to carry out some purification of the solvent before it is

Figure 4.73

Schematic of Pu Ionex Treatment

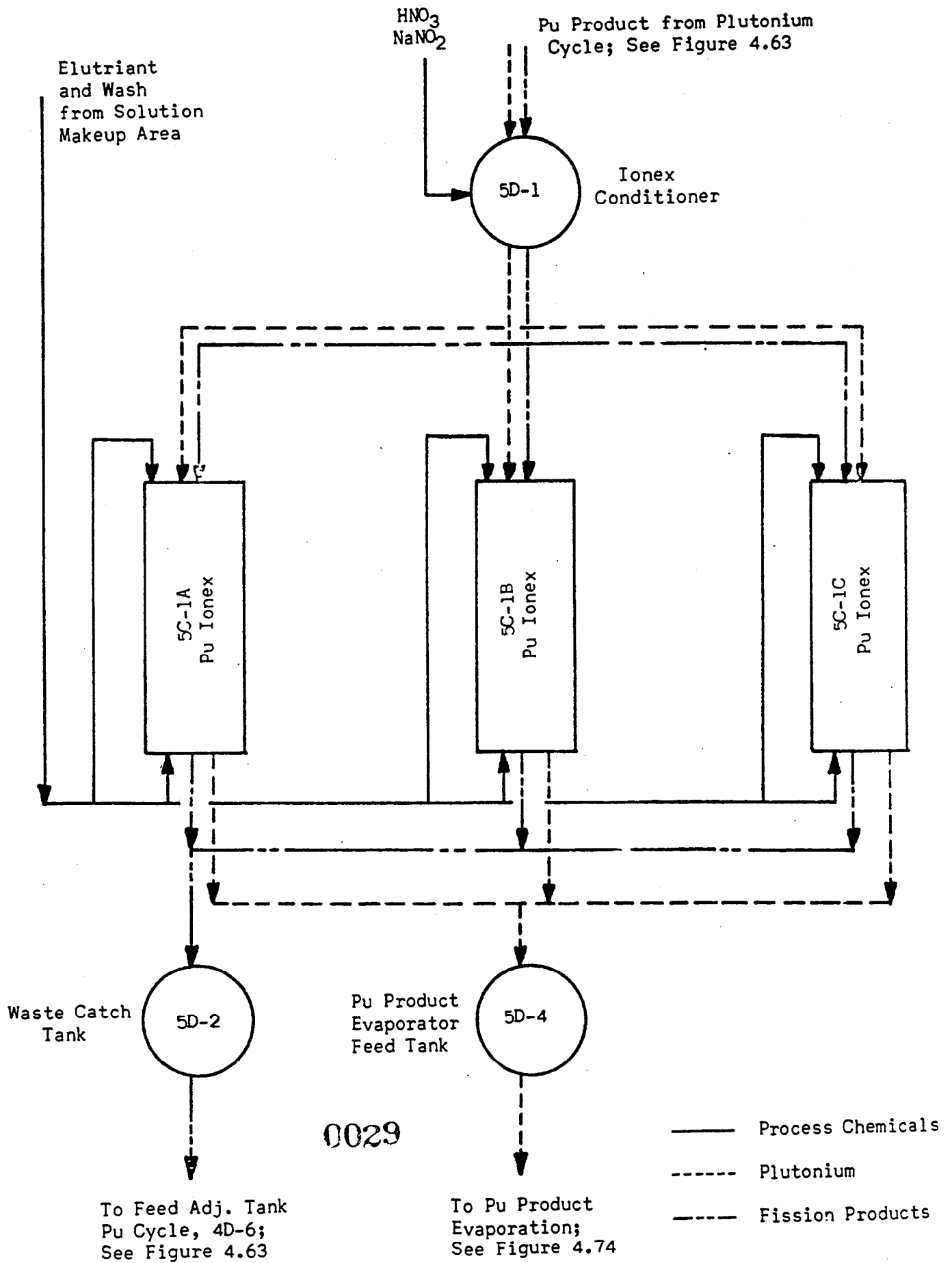
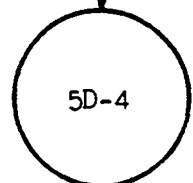


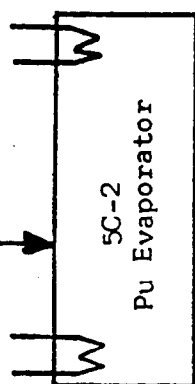
Figure 4.74

Pu Product Evaporation

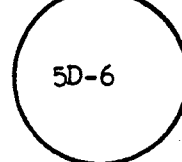
From Pu Ionex;
See Figure 4.73



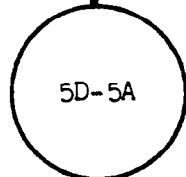
Evaporator
Feed Tank



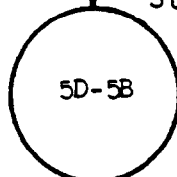
Evaporator
Condensate
Tank



To Tank
4D-8 or
5D-4; see
Figure 4.73

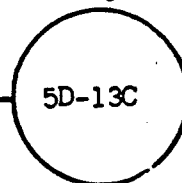


Pu Product



Storage Tanks

Off-Specification
Pu Storage Tank



To Tank
5D-1
See
Figure
4.73

To Pu Product Packaging & Shipping

———— Process Chemicals

----- Plutonium

reused. The most generally used solvent cleanup process, and the one chosen for this plant, is to wash the solvent first with sodium carbonate and then with dilute nitric acid. Sodium carbonate removes traces of metal salts and also is effective in removing DBP. Carbonate, rather than caustic, is used to avoid precipitation of uranium. The nitric acid wash neutralizes any residual carbonate and a cleaner separation between the phases can be made in acid, rather than alkaline solution. The aqueous washes are evaporated in the low level waste evaporator (see Paragraphs 4.83 and 4.84).

4.77 There are three identical sets of solvent washing equipment used for solvent washes of differing activity levels. A schematic flowsheet for the first set, generally used for treating partition cycle solvent waste, is shown in Figure 4.77. Except for differing equipment numbers the other two sets are identical and they are not separately illustrated. However, in Table 4.77 the routing of each solvent waste stream for each of the fuels is indicated.

4.78 Waste solvent from the partition cycle is pumped into the bottom of the carbonate wash column (VC2-13C-1) wherein it is contacted countercurrently with sodium carbonate. The overhead solvent is pumped into the solvent washer (XC2-13D-1) with UWA-13G-1 wherein it is given a batch countercurrent contact with 0.2 M Na_2CO_3 which is pumped in from the solution make-up area and recirculated with pump UWA-13G-2. The overflow from the first stage of 13D-1 goes into a second wherein it is given a second wash. Carbonate coming out of the first stage of the washer is fed to the top of the carbonate wash column. The solvent overflows into the bottom of the acid wash column (XC2-13C-4) wherein the solvent is contacted countercurrently with 0.1 M HNO_3 . Both the carbonate and acid washes are collected in a waste catch tank (LWC-13D-7) from which it is sent to the solvent waste hold tank (LWC-13D-8). After sampling and analyses this waste is sent to the feed tank for the low level evaporator located in the CPC. The washed solvent is returned to the process stream from which it came or it may be sent to the solvent clean up and waste organic catch tank and hence to organic storage tanks.

4.79 The composition of the solvent will have to be adjusted for the various flowsheets. Solvent of 5, 10, and 30 volume per cent TBP will ordinarily be used. Separate storage tanks 13D-15, 16, and 17 are provided to contain these various compositions. Each tank will contain the process inventory required for each solvent composition.

Acid Recovery

4.80 All of the aqueous waste streams from the process contain quantities of nitric acid which must be neutralized before storing the wastes in the steel waste tanks. The quantity of tankage which must be provided for this storage, in most instances, is determined by the

Figure 4.77

First Solvent Wash Cycle - Typical

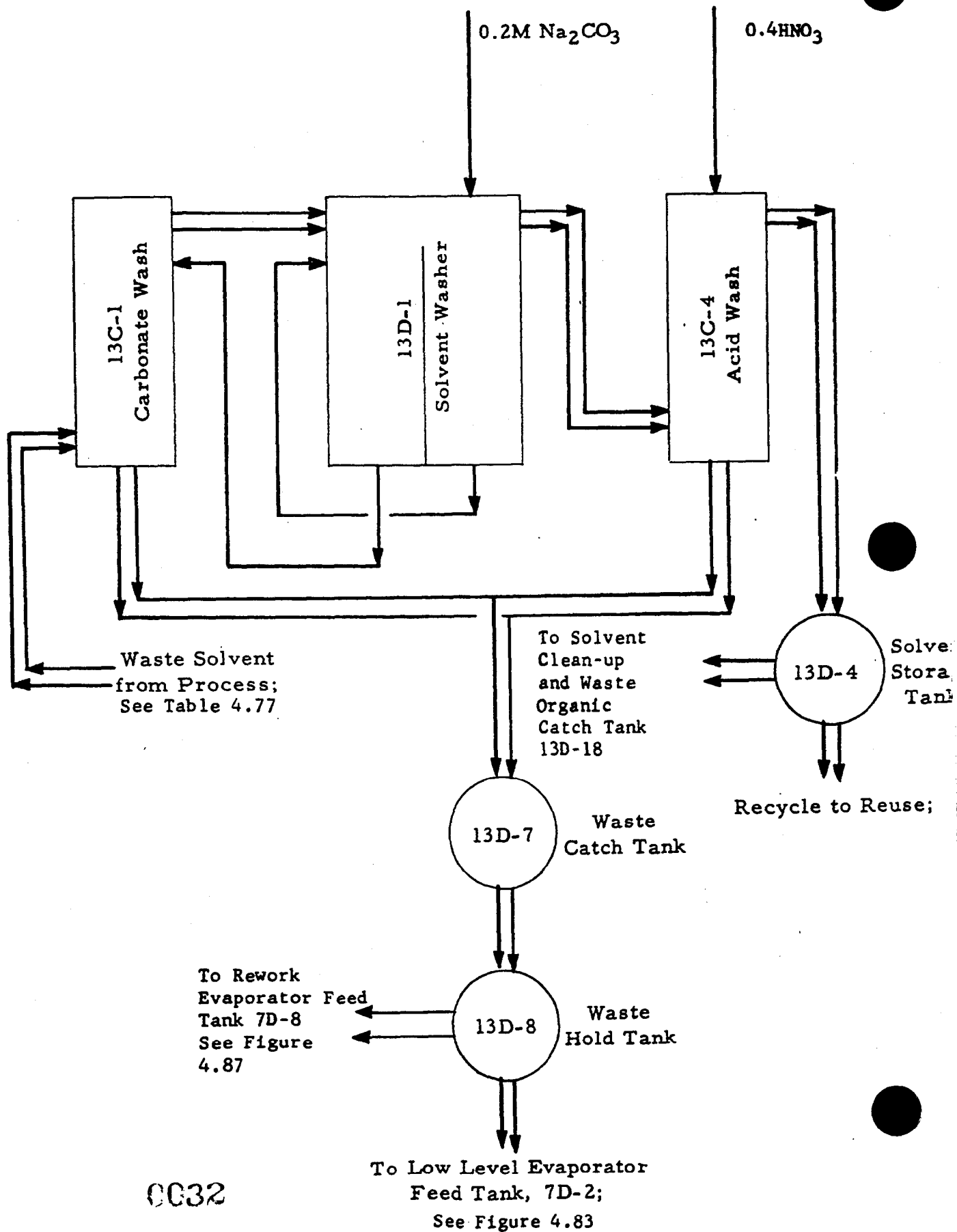


Table 4.77

Solvent Waste Treatment Schedule for Various Fuels

	HCW	ICW	IEW	IIBW
<u>Yankee</u>				
TBP %	30	30	30	30
Solvent Wash Set	1	2	3	1
<u>Commonwealth Edison</u>				
TBP %	30	30	30	30
Solvent Wash Set	1	2	3	1
<u>Northern States Boiler</u>				
TBP %	30	30	30	30
Solvent Wash Set	1	2	3	1
<u>Consolidated Edison</u>				
TBP %	5	5	5	--
Solvent Wash Set	1	2	3	-
<u>PRDC Core</u>				
TBP %	10	10	10	10
Solvent Wash Set	1	2	3	1
<u>Piqua</u>				
TBP %	30	30	30	30
Solvent Wash Set	1	2	3	1
<u>Scrup</u>				
TBP %	30	30	30	30
Solvent Wash Set	1	2	3	1
<u>Zr-U Alloy</u>				
TBP %	10	10	10	--
Solvent Wash Set	1	2	3	-
<u>Al-U Alloy (MTR)</u>				
TBP %	5	5	5	--
Solvent Wash Set	1	2	3	-

Revision 1, October 29, 1962
Revision 2, May 30, 1964

solids content of the waste and this, in turn, is determined by the amount of nitric acid which must be neutralized. It is, therefore, highly desirable to recover and reuse nitric acid from the wastes, not to save the cost of the acid, but to reduce the solids loading in the waste tanks. Two waste evaporators are provided; one for the partition cycle wastes, the other for a second evaporation of the overhead from the first plus all of the remaining aqueous wastes from the solvent extraction processing. Finally an acid fractionator is provided to concentrate the acid to reuseable concentrations.

4.81 A schematic representation of the high level waste evaporation system is shown in Figure 4.81. Waste from the partition cycle or from the rework evaporator can be transferred into the high level waste evaporator feed tank (XC1-7D-1). From here it may be introduced into the high level evaporator (CPC-7C-1) either by air lift or jet. This evaporator is made of stainless steel except for the heat transfer tube bundle which is made of titanium. Because this unit is expected to be subject to the severest corrosion attack in the plant, it is located in the CPC where it may be maintained or replaced remotely. It will be operated with the still bottoms at an acid concentration no greater than 8 M HNO_3 . The unit is described in detail in Section V.

4.82 Overheads from the evaporator are collected in the feed tank for the low level evaporator (LWC-7D-2). The evaporator bottoms represent the concentrated high level waste from the plant. This stream is collected in the high level waste accountability and neutralizer tank (CPC-7D-4) wherein a final sample is taken for purposes of record. After analytical results are available, caustic is added from the solution make-up area and the remaining acid is neutralized. Another sample is taken to insure that the solution is alkaline before it is pumped to the tank farm for storage in the high level waste storage tank (WTF-8D-1).

4.83 In the low level evaporator system the overheads from the high level evaporation, the aqueous waste streams from all of the solvent extraction steps except the partition cycle, and the aqueous solvent washes are evaporated in a manner similar to that used for the high level waste. A schematic representation of the low level evaporation cycle is shown in Figure 4.83. Wastes from all of the solvent extraction cycles except the partition cycle and overheads from the rework or high level evaporators are collected in the low level evaporator feed tank (LWC- 7D-2). From here it is jetted or air lifted into the low level evaporator (CPC-7C-2). This evaporator is made of stainless steel except for titanium heat transfer tube bundles. Even though the activity level in this unit is much less than that in the high level evaporator, the corrosion and maintenance requirements are such that it is located in the CPC where it may be maintained or replaced remotely. It will be operated with the still bottoms at an acid concentration no greater than 8 M HNO_3 .

Revision 1, October 29, 1962
Revision 2, May 30, 1964

Figure 4.81
Schematic High Level Waste Evaporation

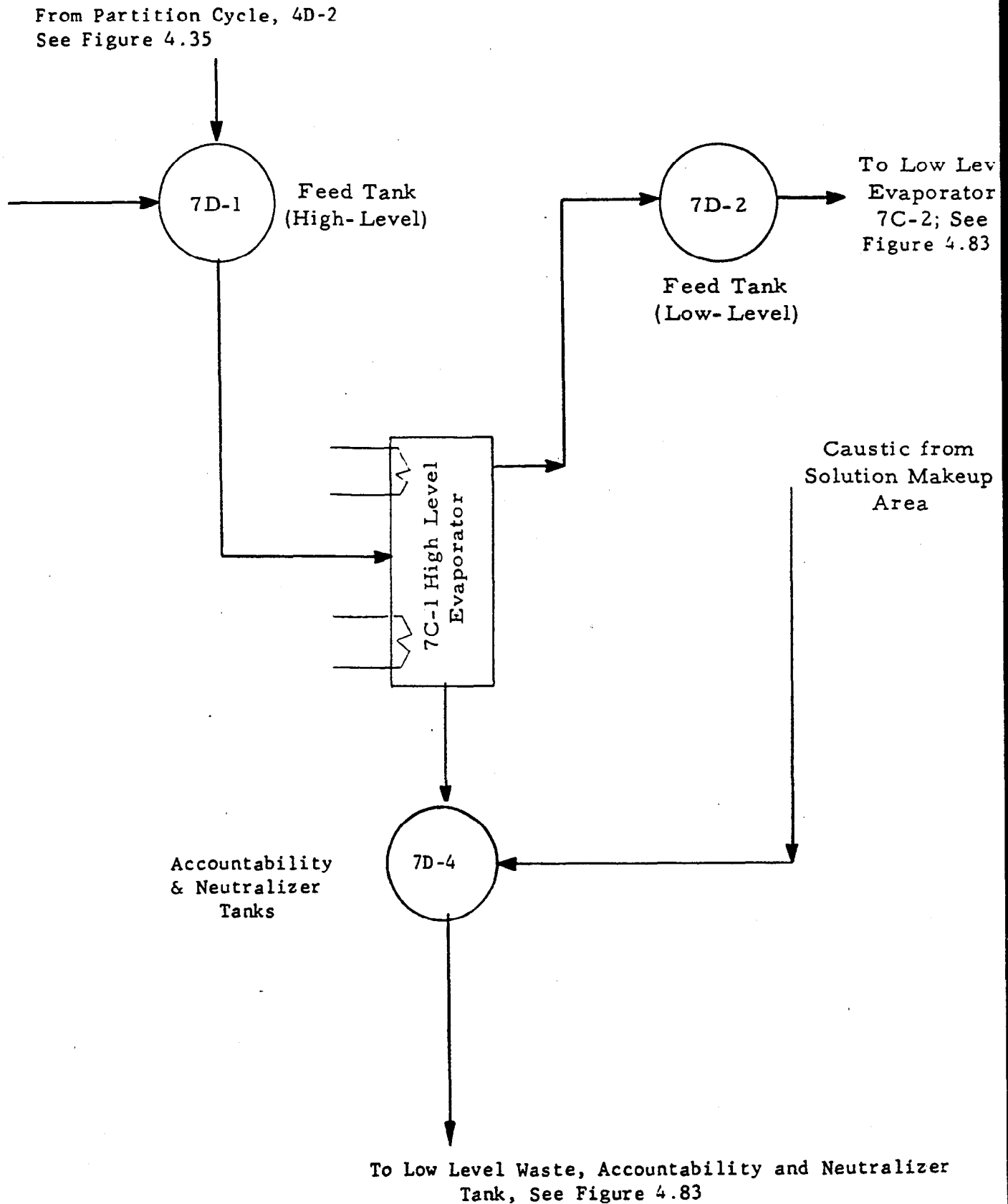


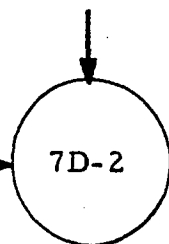
Figure 4.83

Schematic Low Level Waste Evaporation

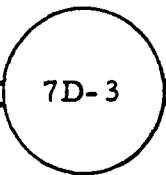
From Plutonium & Uranium Cycles;
See Figures 4.67A and B, 4.63, 4.57 & 4.52

From Solvent
Wash; See
Figure 4.77

From Rework
& High Level
Evaporators
and off-Gas
Scrubbers;
See Figures
4.87, 4.81
& 4.26

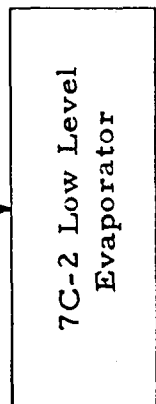


Feed Tank
(Low-Level)



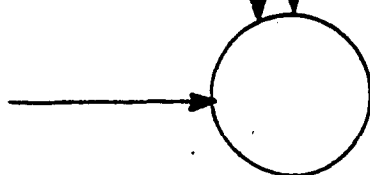
Feed Tank Acid
Fractionator

To Acid
Fractionat:
See Figur
4.85



Caustic from
Solution Makeup Area

From 7D-4, High Level
Waste, Accountability,
Neutralizer tank;
See Figure 4.81



Rework Evaporator
Feed Tank 7D-8;
See Figure 4.87

0036

To Low Level Waste Storage,
8D-2

4.84 Overheads from the evaporator are collected in the feed tank for the acid fractionator (OGC-7D-3). The evaporator bottoms are collected in the low level waste accountability-neutralizer tank (CPC-7D-10) wherein a final sample is taken for purposes of record. After analytical results are available, caustic is added from the solution make-up area and the remaining acid is neutralized. Another sample is taken to assure that the solution is alkaline before it is pumped to the tank farm for storage along with the high level waste in the high level waste storage tanks (WTF-8D-1).

4.85 In the acid fractionation system, the overhead from the low level evaporator, which contains all of the recovered acid decontaminated from most of the radioactivity associated with the original waste streams but at nitric acid concentration too low for reuse, is put into an acid fractionating column which produces an overhead of weak acid (about 0.002 M HNO_3) and a still bottom of 12 M HNO_3 . A schematic representation of this is shown in Figure 4.85.

4.86 Overhead condensate from the low level evaporator, collected in the acid fractionation feed tank (OGC-7D-3), is pumped (AR-7G-4, 4A) through a feed vaporizer (ARC-7E-1) and then fed as a vapor into the middle of the acid fractionator (AR-7C-3). A bottoms fraction is taken from the vaporizer and collected either in the hot acid storage tank (HAC-7D-11) or the hot acid batch tank (HAC-7D-12) from either of which it may be pumped (HAC-7G-3) to the dissolvers. The acid fractionator is a sieve plate column, 30 inches in diameter at the bottom and 54 inches in diameter at the top. It is 28 feet 10 inches tall. Overhead (0.002 M HNO_3) is collected in the weak acid catch tank (ARC-7D-6) from which it is sent to the general purpose evaporator (7C-5) or to the Lagoon via the interceptor. Strong acid (12 M) is taken from the bottom of the column and collected in a recovered acid storage tank (SST-7D-5) from which it may be pumped (SST-7G-2) to the recovered acid header in the solution make-up area.

Rework System

4.87 Solvent extraction is a process which is well understood and upon which a great deal of work has been done and information accumulated. Consequently, it is expected that most of the time the process will work as expected and the losses will be acceptably low. However, the product being recovered is of high unit cost and the acceptable loss is, therefore very low. It is only prudent to assume that occasionally losses will be higher than are desirable and to provide a means of handling this situation. All waste streams are sampled and analyzed before discard to the waste disposal system. If at any time it is found that a waste stream contains more product than can be economically discarded, that stream will be sent to the rework system. A schematic of that system is shown in Figure 4.87. The system consists of a rework evaporator feed tank (XC1-7D-8) to which can be routed any of the aqueous waste streams. From this tank the stream is jetted to the rework evaporator (CPC-12C-1).

Figure 4.85

Schematic of Acid Fractionator

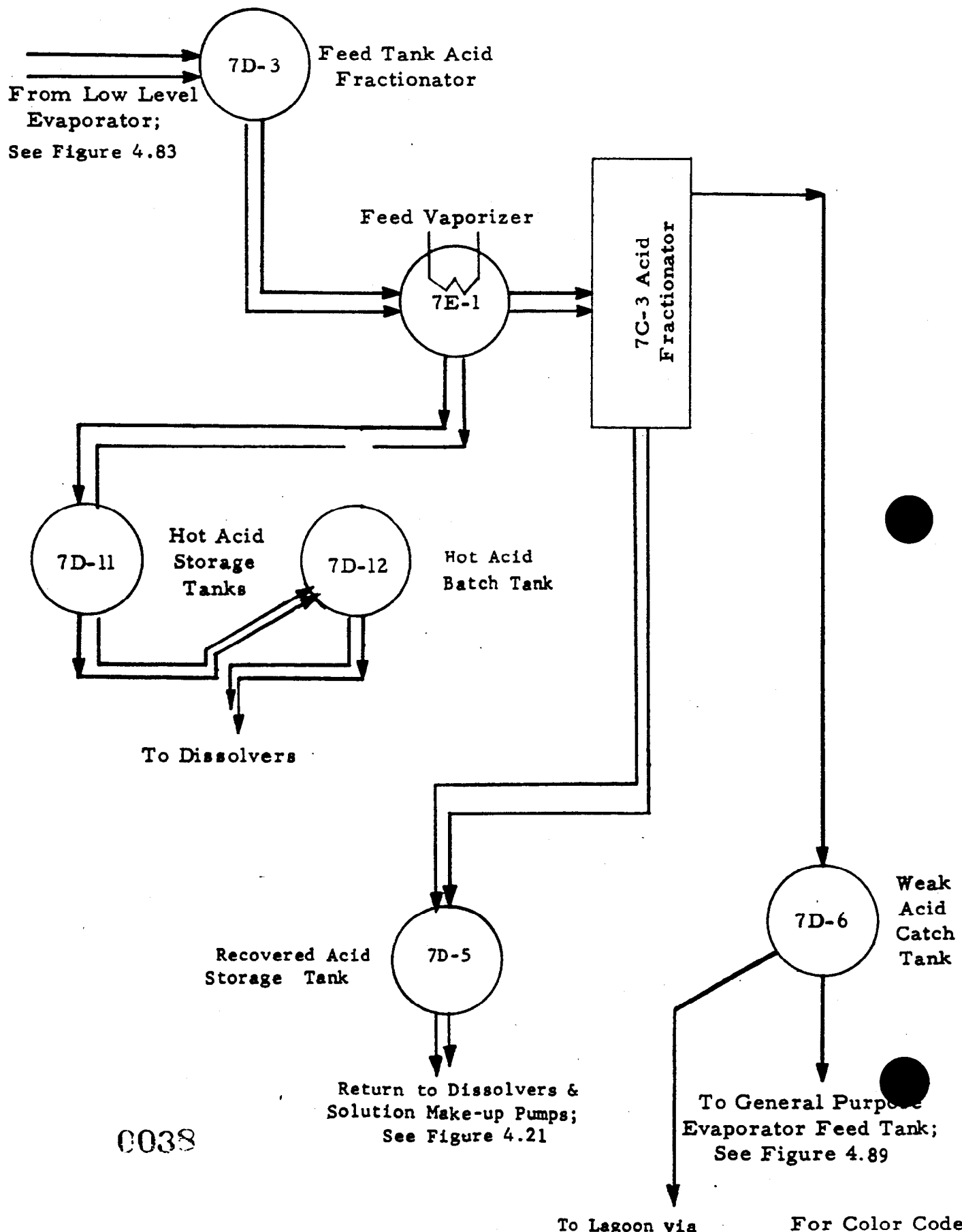
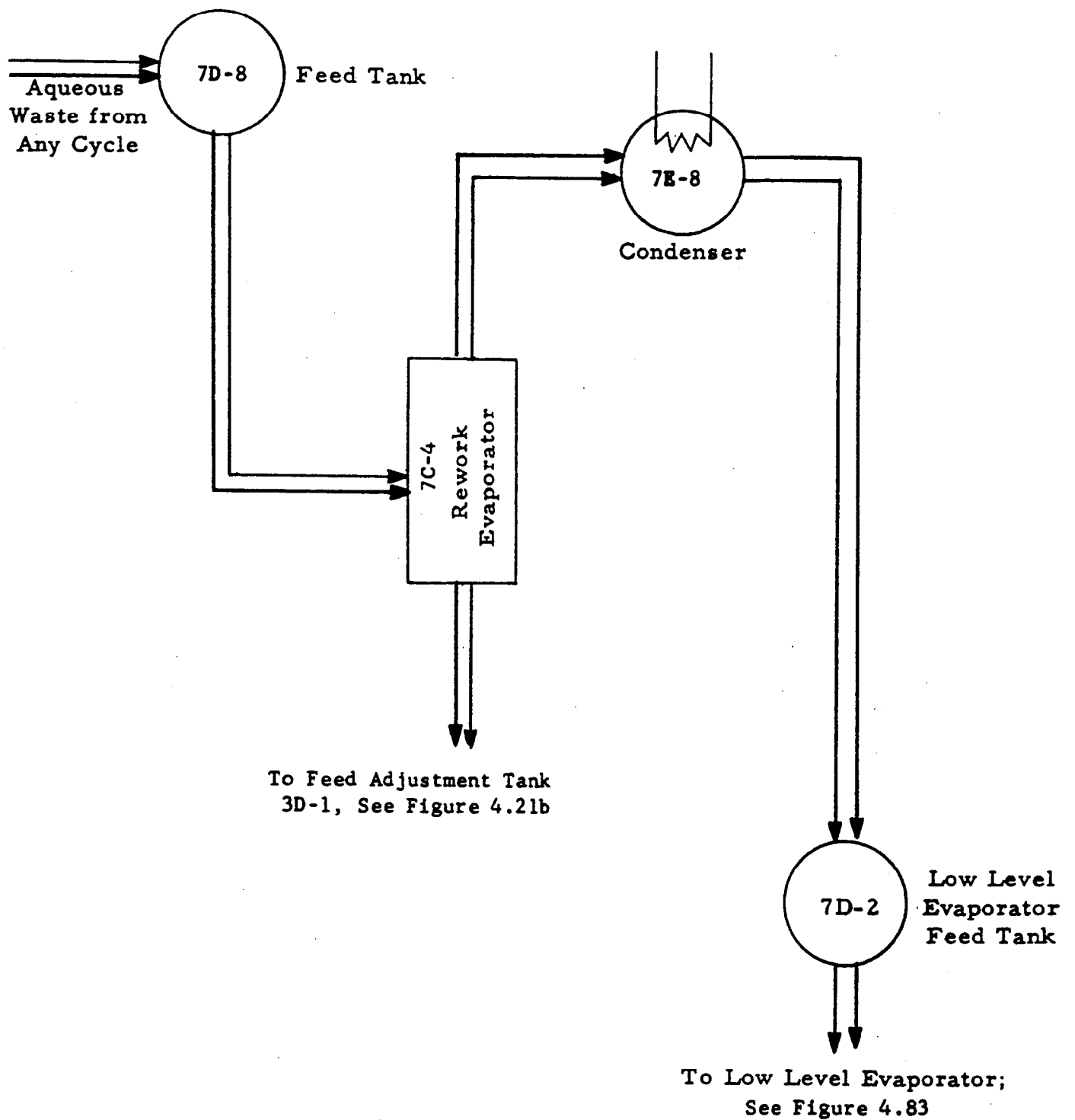


Figure 4.87
Schematic of Rework System



0039

For Color Code

Figure 4.89

Schematic General Purpose Evaporator

